PB-224 243

CHARACTERIZATION OF PARTICULATES AND OTHER NON-REGULATED EMISSIONS FROM MOBILE SOURCES AND THE EFFECTS OF EXHAUST EMISSIONS CONTROL DEVICES ON THESE EMISSIONS

James E. Gentel, et al

Dow Chemical Company

Prepared for:

Environmental Protection Agency

March 1973

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PB 224 243

APTD-1567

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF AIR AND WATER PROGRAMS
MOBILE SOURCE AIR POLLUTION CONTROL
EMISSION CONTROL TECHNOLOGY DIVISION
ANN ARBOR, MICHIGAN 48105

MARCH 1973

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CONTRACT NUMBER: EHS-70-101

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Prepared For
U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Water Programs
Mobile Source Air Pollution Control
Emission Control Technology Division
Ann Arbor, Michigan 48105

March 1973

BIBLIOGRAPHIC DATA SHEET

1. Report No. APTD-1567

2. /

3. Recipient's Accession No. PB-224 243

4. Title and Subtitle

Characterization of Particulates and Other Non-Regulated Emissions from Mobile Sources and the Effects of Exhaust Emissions Control Devices on These Emissions

5. Report Date March 1973

6.

7. Author(s) J. E. Gentel, O. J. Manary, Joseph C. Valenta

8. Performing Organization Rept. No.

9. Performing Organization Name and Address

The Dow Chemical Company
Midland, Michigan 48640

10. Project/Task/Work Unit No.

11. Contract/Grant No. EHS-70-101

12. Sponsoring Organization Name and Address

U.S. ENVIRONMENTAL PROTECTION AGENCY
Mobile Source Air Pollution Control
Emission Control Technology Division
Ann Arbor, Michigan 48105

13. Type of Report & Period Covered

14.

15. Supplementary Notes

16. Abstracts The effect of emission control devices on the particulate emissions of an automotive power plant was investigated. The work was divided into five tasks as follows: TASK I was the characterization of a particulate trapping system, and the determination of what effects, if any, were noted as conditions within the system were controllably varied; TASK II was the definition of a particulate baseline for a 1972 400 CID engine, using non-leaded and low lead fuel - no emission control devices were used for the baseline runs; TASK III was the evaluation of the particulate emissions from a 1972 400 CID engine equipped with the following control devices - three different oxidation catalysts, one NOx catalyst, and one exhaust gas recirculation system; TASK IV involved testing automobiles equipped with control devices for particulate emissions - these vehicles were supplied by both the contractor and the Government; and TASK V was to define a preliminary collection system for diesel engine particulate sampling. In all tasks, particulate mass emission rates were measured, as well as particle mass size distribution, carbon and hydrogen, trace metal, and benzo-a-pyrene content of the particulate. Ammonia and aldehydes were measured in the exhaust gas condensate, and gaseous emissions were determined as a routine check on engine operating conditions.

17. Key Words and Document Analysis. 17a. Descriptors

Air pollution
Particles
Exhaust emissions
Air pollution control equipment
Gas sampling
Catalytic converters
Spark ignition engines
Diesel engines

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group 13B

18. Availability Statement Unlimited

19. Security Class (This Report) UNCLASSIFIED

20. Security Class (This Page UNCLASSIFIED

21. No. of Pages ~~216~~ 217

22. Price 13.00

FORM NTIS-35 (REV. 3-72)

THIS FORM MAY BE REPRODUCED

USCOMM-DC 14952-P72

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This report was furnished to the U.S. Environmental Protection Agency by The Dow Chemical Company, Midland, Michigan 48640 in fulfillment of Contract Number EHS-70-101. The contents of this report are reproduced herein as received from The Dow Chemical Company. The opinions, findings, and conclusions expressed are those of the author and not necessarily those of the Environmental Protection Agency.

Office of Air and Water Programs Publication Number APTD-1567.

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FINAL REPORT

CHARACTERIZATION OF PARTICULATES AND OTHER NON-REGULATED EMISSIONS FROM MOBILE SOURCES AND THE EFFECTS OF EXHAUST EMISSIONS CONTROL DEVICES ON THESE EMISSIONS

Government Contract
EHS 70-101

March, 1973

FOREWORD

This report was prepared by the Transportation Chemicals Research Group, Ag-Organics Department, The Dow Chemical Company, Midland, Michigan, under Contract EHS 70-101. The work reported herein was administered under the direction of the Office of Air and Water Programs, Environmental Protection Agency, with Dr. Robert E. Sampson and Mr. Chas. L. Gray, Jr. serving as Project Officers.

The report covers work performed from Sept. 1, 1971, to Dec. 31, 1972.

The authors of this report are James E. Gentel, Otto J. Manasry, and Joseph C. Valenta.

The authors wish to acknowledge the significant contributions of the following individuals:

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N. J. Smith
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B. Coleman
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ABSTRACT

This report describes work carried out on a research program to determine the effect of emission control devices on the particulate emissions of an automotive power plant. The work was divided into five tasks as follows:

TASK I was the characterization of a particulate trapping system, and the determination of what effects, if any, were noted as conditions within the system were controlably varied.

TASK II was the definition of a particulate baseline for a 1972 Pontiac 400 CID engine, using non-leaded and low lead fuel. No emission control devices were used for the baseline runs.

TASK III was the evaluation of the particulate emissions from a 1972 Pontiac 400 CID engine equipped with the following control devices:- three different oxidation catalysts, one NO_x catalyst, and one exhaust gas recirculation system.

TASK IV involved testing automobiles equipped with control devices for particulate emissions. These vehicles were supplied by both the contractor and the Government.

TASK V was to define a preliminary collection system for diesel engine particulate sampling.

In all tasks, particulate mass emission rates were measured, as well as particle mass size distribution, carbon and hydrogen, trace metal, and benzo-α-pyrene content of the particulate. Ammonia and aldehydes were measured in the exhaust gas condensate, and gaseous emissions were determined as a routine check on engine operating conditions.

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I. INTRODUCTION

The work presented in this report covers the second half of contract EHS 70-101. In the previous work, reported in a final report dated July 1971, some preliminary studies were made on the effect of emission control devices on unregulated emissions. The extension to Contract EHS 70-101, which is reported here, involved a more detailed look at specific control devices and the resulting effects on particulate size and mass, particulate composition, and condensate composition. The work was divided into five specific tasks in order to smoothly carry out the technical goals of the contract.

The major objective of Task I was to study the effect of specific engine and sampling variables on certain non-regulated emissions under highly controlled conditions. Studies were made on non-leaded and low lead fuels.

During the course of some preliminary studies undertaken in the previous year's work on Contract EHS 70-101, alarming differences were noted in the mass of particulate emitted when non-leaded fuel was used, and when the filtering systems and dilution tube were operated at different flow rates and temperatures. In order to reach an understanding of the above effects, and to define a meaningful set of sampling parameters, a study was made of a number of sampling variables and their effect on the mass of particulate matter collected at a filter.

Task II involved running a 400 CID Pontiac engine, using non-leaded and low lead (0.5 cc/gal) fuels, to determine a baseline for subsequent studies. Operating conditions were varied and included rich, standard, and lean air/fuel ratios, as well as advanced, standard, and retarded spark timing. The sampling techniques settled upon in Task I were used to collect particulate.

The objective in Task III was to evaluate various emission control devices with respect to their effect on non-regulated emissions. The devices tested under this portion of the contract include:

Three oxidation catalysts
One reduction catalyst
One exhaust gas recirculation system

Initially, work was done using both non-leaded and low lead (0.5 cc/gal) fuels. The leaded fuel itself caused increases in the amount of particulate and, after testing one catalyst on leaded fuel, the rest were run only on non-leaded fuel. The low lead fuel poisoned the catalyst sufficiently so that it was felt that future runs would be more meaningful if only non-leaded fuel was used.

The devices were obtained from either the manufacturer or an automobile company under a secrecy agreement, to protect any proprietary rights involved. Consequently, the data on the devices are reported with the only reference to the device being a code letter.

Task IV was an evaluation of the particulate emission levels of vehicles equipped with various control devices. Several of these vehicles were made available to Dow by the manufacturer, while others were supplied by the Government for testing. Ten different vehicles were tested, with 19 runs made on the 10. Each vehicle is discussed in detail in the Experimental Section of Task IV.

Task V was a limited diesel engine study to establish baseline data for emissions present in the exhaust. Due to an increased emphasis on the vehicle studies, this task was only partially completed.

II. CONCLUSIONS

1. The use of three different oxidation catalysts on an engine stand, with non-leaded fuel, increased the amounts of particulate collected at 60 mph by a factor of 2-5, compared to a baseline run, except under rich air/fuel ratios. Two catalysts did not generally increase the particulate collected at 30 mph, or under cyclic conditions, while an increase was noted with one catalyst under both conditions. The total particulate collected from the control devices was less than normally found when using 3 cc leaded fuel.

2. There was no evidence in the particulate of catalyst degradation being the cause of the increase in particulate mass.

3. The mass medium equivalent diameter was shifted significantly toward smaller particles, when compared to the baseline, for all of the catalysts tested on an engine stand.

4. In almost all cases, 30 mph at steady-state, on an engine with no control devices, gave higher particulate levels than the corresponding 60 mph run.

5. An increase in particulate comparing 30 mph to 60 mph was noted during the baseline runs. This appeared to be reversed when running at standard conditions with two of the three oxidation catalysts.

6. The three oxidation catalysts significantly lowered the emission of aldehydes, as collected in the condensate, as well as lowering the total hydrocarbons.

7. The vehicles on which mileage accumulation tests were made exhibited a large degree of fluctuation with respect to grams/mile as a function of mileage. No clear trends have been established.

8. The precision of measuring particulate mass from a vehicle exhaust is substantially lower than that of measuring an engine stand run, probably due to differences in operating conditions prior to the tests.

9. In general, the particulate matter which exhibited higher percentages of carbon also exhibited higher parts per million of benzo-α-pyrene.

10. The mass medium equivalent diameter became larger with mileage for two of the three mileage accumulation cars, while decreasing for the other.

11. The mass medium equivalent diameter for the device equipped vehicles in general correlates well with the numbers obtained during the engine stand runs, even though the overall mass of particulate changed.

12. In general, the low lead fuel gave higher particulate levels, in grams/mile, than the non-leaded fuel.

13. Overall, the aldehyde content of the exhaust condensate was not significantly different between the non-leaded and low lead fuel.

14. Under rich air to fuel ratio conditions, both the oxidation catalysts and the reduction catalyst gave a significant increase in NH_3 emissions.

15. The concentration of benzo-α-pyrene in the particulate varied widely with engine conditions, but did not appear to be significantly changed by use of leaded vs. unleaded fuel.

16. Air/Fuel ratio had an effect on particulate with the standard setting generally being lower than either rich or lean settings.

17. The effect of particulate due to changes in spark timing was sporadic and, therefore, inconclusive based on this data.

18. Different temperatures at the filter and the sample probe caused differences in amounts of particulate collected.

19. Changes in flow rate through the dilution tube caused slight variations in the amounts of particulate collected.

20. Dilution air temperature proved to be important since a lower temperature showed definite increases in the amount of particulate collected.

21. Sample probe location appeared to have only very small effects on particulate samples.

22. Face velocity of a sample stream through a given filter was important in that more sample, comparatively, tended to be collected at lower face velocities.

23. A majority of the sample during a steady-state run was collected within the first 25 percent of the time period over which the run was made.

24. Absolute measurements of grams/mile are misleading when measured during a steady-state run of long duration for the reason given in 23 above. Comparisons can be made, however, between runs of like time periods, and are valid as measurement of a trend.

25. The modified Federal cycle cold start gave more particulate than the 23 minute Federal cycle.

III. EXPERIMENTAL PROCEDURES

A. PARTICLE GENERATION

1. Engine Dynamometer Studies

The engines used in this study were 1972 Pontiacs, 400 CID. These engines were mounted on the dynamometer bed plate and attached to a fully instrumented Eaton Dynamatic dynamometer. Appropriate control and sensing devices were attached to the engine. The following procedure (Table 1) was then employed to run-in the new engines, using Indolene low lead (0.5 cc/gal) fuel.

TABLE I

NEW ENGINE BREAK-IN PROCEDURE
(28 hours)

1) Warm up engine to 180°F coolant outlet temperature at 1000 rpm, no load. Set spark advance and best idle according to manufacturer's specifications.
2) Run one hour at 1500 rpm, no load, automatic spark advance and fuel flow. Shut down, retorque cylinder heads, drain and change lubricating oil.
3) Run Cycle 1

RPM	Man. Vac. (In. Hg)	Time (Hr)
1500	15.0	1.0
2000	14.0	1.0
2400	14.0	1.0
2600	14.0	1.0
2000	11.0	1.0
		5.0

4) Run Cycle 2

RPM	Man. Vac. (In. Hg)	Time (Hr)
1500	7.0	0.2
2000	7.0	0.6
2500	7.0	1.0
3000	7.0	1.0
2000	7.0	0.2
		3.0

5) Repeat Cycle 2.

6) Run Cycle 3

RPM	Man. Vac. (In. Hg)	Time (Hr)
2000	WOT*	1.0
2500	WOT	1.0
3000	WOT	1.0
3500	WOT	0.5
2800	WOT	0.5
		4.0 x 4 cycles = 16 hours

*WOT - wide open throttle

7) While engine is hot, run motoring compression and conduct leak-down check.

The engine was removed from the dynamometer, drained, partially dismantled, cleaned, reassembled, and placed back on the dynamometer stand. A manufacturers original standard vehicle exhaust system for the specific test engine was attached to one bank of cylinders. The other bank of cylinders was attached to the dynamometer cell exhaust system. Suitable engine monitors were attached to the engine in order to provide continuous monitoring of oil pressure and temperature, coolant temperature, carburetor air flow rate (using a Meriam Laminar Flow Element 50MC-2-45F) and temperature, etc.

The engine was then run for 75 hours using the following "conditioning" sequence (Table 2) employing the specific test fuel designated for that run. This sequence of testing was used for the initial break-in of the engine, as well as for certain emission tests. It was not run prior to evaluation of each condidate emission control device. During the conditioning sequence, total unburned hydrocarbons, oxygen, nitrogen, carbon monoxide, carbon dioxide, and oxides of nitrogen were measured at frequent intervals by FID, gas chromatography, chemical absorption, and a Scott NO/NO_2 analyzer, respectively. Air/fuel ratios were also calculated based upon exhaust gas composition.

TABLE 2

TEST ENGINE CONDITIONING SEQUENCE

Cycle	RPM	Time (Min.)	Vac. (In. Hg)	Decay
1	800	2	18.8	--
2	1070	13	16.4	1/2 min.
3	1615	20	17.2	1/2 min.
4	2125	13	14.3	1/2 min.
5	1070	12	16.4	1/2 min.

Sequence repeats after each five cycles.

Following the conditioning sequence, the engine exhaust system was attached to the dilution tube inlet pipe and the system was ready for experimental particulate sampling. All subsequent runs were 60 mph or 30 mph 2-hour steady-state runs.

2. Chassis Dynamometer Procedures

A Clayton CT-200-0 chassis dynamometer with a variable inertia flywheel assembly was used in all tests conducted under this program. A Chelsa direct-drive Model PLDUP-300A fan was located in front of the test vehicle, and operated at 1750 rpm providing 5,000 scfm air flow. In these tests, the vehicle was operated under approximately 60 mph road-load cruise conditions (2250 rpm - 17" Hg manifold vacuum) and under cyclic conditions of the Federal Test Procedure (old California cycle) and LA-4 procedure driven by a vehicle operator following the cycle on a strip-chart recorder driver aid.

Table 3 indicates specific procedures employed to prepare each vehicle for test run.

TABLE 3
VEHICLE TEST PROCEDURE - CHASSIS DYNAMOMETER

1) General Vehicle Inspection

Exhaust System:

a) Inspect for holes or cracks, dents, and collapse
b) Inspect for leaking joints

Engine, check

a) All fluid levels
b) All coolant hoses
c) Air pump fan, power steering, and belts
d) Check heat riser (if applicable) for fullness of operation
e) Check automatic choke operation and adjustment, where possible

2) Engine Analysis and Tune-up

Scope Check

a) Start engine and allow to warm up for at least 15 minutes
b) With engine running at fast idle, check
    - Spark plugs
    - Spark plug wires
    - Distributor cap and rotor
    - Coil output
    - Points

TABLE 3 (continued)

c) With engine running at idle, check
    - Dwell
    - Timing

d) With engine running at 1500 and 2400 rpm, check timing device

e) Carburetor Adjustment
    - Tighten intake manifold and carburetor
    - Install new air cleaner element
    - With engine running at specified idle speed, adjust air to fuel ratio to specifications
    - Make final adjustment on idle speed

f) Recheck all scope patterns for normal appearance

3) Instrumentation and Equipment Installation

Vacuum and RPM monitors

a) attach tachometer to ignition coil
b) connect "U" tube monometer to intake manifold
c) install throttle cable (if running under cruise mode)

Wheels

a) remove rear wheels
b) Install test tires and wheel assemblies

4) Procedure for Cold, Hot Starts, and Engine Temperature Stabilization

Cold Start

a) Place vehicle on the dynamometer rolls, set inertia weights for specific vehicle, and go through the preparation for test as well as the tune-up procedure.

b) Allow at least a 12-hour soak period, but not more than 16 hours.

c) Connect vehicle tailpipe to dilution tube.

d) Start the vehicle and proceed with the individual test.

Hot Start

Continuation of the cold start only after the engine temperature has stabilized.

TABLE 3 (continued)

Engine Temperature Stabilization

Two-hour steady state runs were made only after a cold start and one or more hot starts. Thus, the engine and particle collecting system were always at operation temperature before the steady state sampling was begun. When preparation has been completed, the vehicle is placed in gear and the speed is increased to 2250 rpm with the intake manifold vacuum is set at 17.0" Hg by controlling the amount of load imposed on the drive wheels. At the time when the load and the speed become stabilized, the tailpipe is connected to the dilution tube inlet pipe and particulate collection is started when dilution tube has come to equilibrium.

The procedures outlined in Table 3 were used whenever possible. On certain vehicle tests where the vehicle was equipped with proprietary systems, only visual checks were made of the components and engine hardware. In some cases, the vehicles were adjusted by personnel from the organization submitting the vehicle for testing.

B. PARTICLE COLLECTION

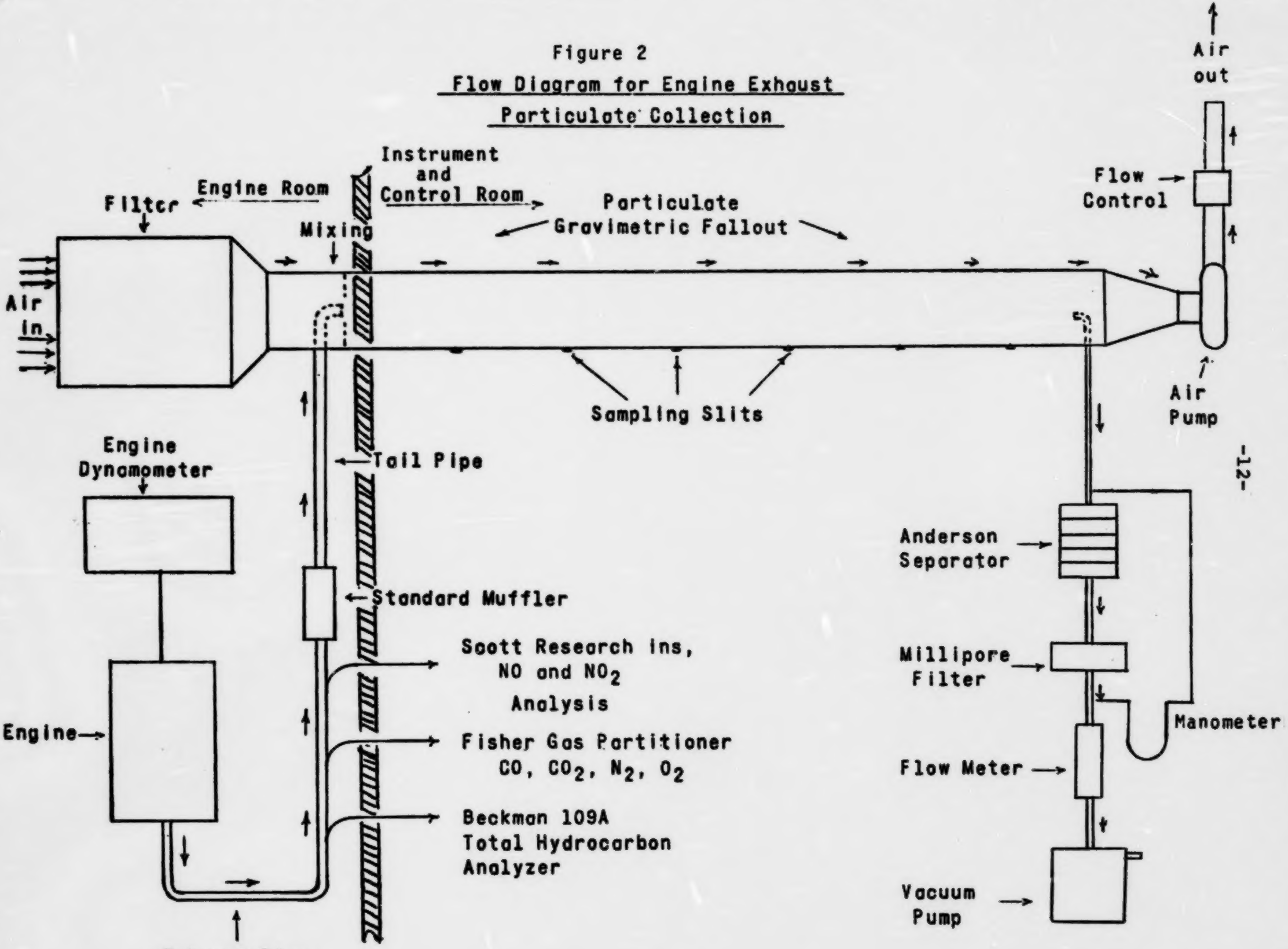
Exhaust particles were collected after air dilution of the exhaust in the large dilution tube described below. During the engine stand studies, one-half of the engine exhaust was fed into the tube while the other half was exhausted through the dynamometer cell exhaust system. With vehicles, the entire exhaust stream was diluted. Using EGR, the tests were conducted using full exhaust.

1. Dilution Tube

Air dilution and cooling of the exhaust was accomplished by a dilution tube 16 inches in diameter and 27 feet in length constructed of extruded polyvinyl chloride (PVC) pipe in several sections with butt joints which were taped during assembly prior to each run (Figure 1). The diluent air coming into the tube is filtered by means of a Dri-Pak Series 1100

Figure 2

Flow Diagram for Engine Exhaust Particulate Collection


Air out
Flow Control
Air Pump
Instrument and Control Room
Engine Room
Filter
Mixing
Air In
Particulate Gravimetric Fallout
Sampling Slits
Engine Dynamometer
Tail Pipe
Standard Muffler
Engine
Exhaust Pipe
Scott Research ins, NO and NO_2 Analysis
Fisher Gas Partitioner CO, CO_2, N_2, O_2
Beckman 109A Total Hydrocarbon Analyzer
Anderson Separator
Millipore Filter
Manometer
Flow Meter
Vacuum Pump

Class II PIN 114-110-020 untreated cotton filter assembly. This filter assembly is 24" x 24" and has 36 filter socks which extend to 36 inches in length. This filter will pass particles 0.3μ in size and smaller. Pressure drop at 600 cfm flow rate is minimal.

Exhaust was delivered to the tube via a tailpipe extension which was brought into the bottom of the tube downstream of the filter assembly. The extension was bent 90 degrees inside the tube, thus allowing the introduction of the exhaust stream parallel to the tube axis. Within the dilution tube, along the perpendicular plane of the end of the exhaust extension was a mixing baffle which has an 8-inch center hole and was attached to the inside diameter of the tube. The baffle presented a restriction to the incoming dilution air in the same plane as the end of the exhaust extension and performed three essential functions.

a) Provided a turbulent mixing zone of exhaust gas and dilution air.
b) Eliminated engine exhaust pulsations in the tube.
c) Caused the tube to perform as a constant volume device over a wide range of engine exhaust output volumes.

2. Sampling Devices

The particulate sampling zone for particles smaller than 15μ is located at the exhaust end of the dilution tube. Four isokinetic sample probe elbows are located in the exhaust-air stream. One probe is connected to an Andersen Impact Sampler Model 0203, a filter assembly, and a vacuum pump, in that sequence. The probes are 0.754 inch ID stainless steel tubes which are located as shown in Figure 1. A mercury manometer is connected between the dilution tube probe and the exhaust side of the filter assembly, to measure the pressure drop across the filter. A flow meter was used to monitor and regulate the flow through the Andersen Sampler during the course of each run. Two sample probes were both connected to 1 cfm Millipore filter holders (142 mm) fitted with Gelman Type A glass fiber filter pads and vacuum pumps. The fourth filter was either a 293 mm, 4 cfm glass fiber; or a 142 mm, 4 cfm glass fiber, the former being used on engine stand runs and the latter on vehicles.

Prior to use, all the filters were stored in the instrument room which is temperature- and humidity-controlled. The filters were placed on the tray of the Mettler Analytical Balance, allowed to reach equilibrium, and then weighed out to 0.1 milligram (mg).

After the test, the filters were removed from the holders and again allowed to reach equilibrium, noted by no further change in weight, and then weighed to 0.1 mg. This was done in the same room in which the papers were stored. The Millipore filter pads used were 142 mm Type AAWP 0.8μ. The glass fiber filter pads used were Gelman 0.3μ Type A.

Andersen Sampler Model 0203 with a back-up 142 mm Millipore filter was used as the basic particle collection device for determining mass size distribution. Sample probes sized to deliver an isokinetic sample from the dilution tube were connected to the Andersen Sampler through which a proportional sample was drawn at 1 cfm. The D_{50} cut-off values for the Andersen stages are listed in Table 4. The D_{50} value is the size at which 50% of those particles are collected, while the remaining 50% pass on through to be collected on the next stage.

TABLE 4

D_{50} VALUE - ANDERSEN MODEL 0203

Stage 1	D_{50}	9μ
Stage 2	D_{50}	5.45μ
Stage 3	D_{50}	2.95μ
Stage 4	D_{50}	1.55μ
Stage 5	D_{50}	0.95μ
Stage 6	D_{50}	0.54μ

Preweighed glass collection plates were used in this study. Back-up filters were either Millipore type AAWP 0.8μ or Gelman 0.3μ Type A 142 mm diameter. Gelman glass fiber filters were routinely used while the Millipore filters were used for special analytical applications.

C. CONDENSATE COLLECTION

Exhaust gas condensate was collected for aldehyde and NH_3 analyses. A tap was placed into the raw exhaust gas stream, as close to the tailpipe of a vehicle as practical (about 12 inches in most cases) and 8 feet from the muffler in an engine run. Raw exhaust was drawn through a three-stage cold trap at the rate of 1 cfm. The cold trap consisted of three flasks connected in series containing 40 grams each of DI water, immersed in an ice water bath. The exhaust gas flow bubbles through the water in the flasks. Condensate was collected for 41 minutes during a modified Federal cycle cold start, and for 23 minutes during a Federal cycle hot start. Sampling was terminated at 25 minutes during a steady state run.

The condensate from the exhaust gas was analyzed for ppm of HCHO and NH_3. It was felt desirable to express this analysis in volume percent to compare to the other components analyzed in the exhaust gas. The procedure for this calculation is as follows:

The "Ideal Gas Law" was used

$$PV = nRT$$

$$PV = \frac{nRT}{P}$$

The total liters of exhaust that was put through the condenser is known. The liters of the aldehyde can be calculated from the formula above, so the volume percent can be calculated. This volume percent is reported as volume parts per million in the exhaust.

D. ANALYTICAL METHODS

Collected exhaust particles have been analyzed for both physical and chemical character. Many analytical techniques have been employed in the past, some of which provide very similar data in the interest of correlating trends observed. This section reviews the basic analytical concepts applied to each of the many test components from fuels to exhaust particles. Detailed descriptions of the specific analytical procedures employed are then presented. Table 5 is a summary of the techniques used on the exhaust emissions.

TABLE 5
ANALYTICAL TECHNIQUES FOR EXHAUST SPECIES

O_2, N_2, CO, CO_2	Fisher Gas Partitioner
Total Hydrocarbons	Beckman Model 109A Flame Ionization Detector.
Oxides of Nitrogen	Beckman UV and IR Analyzer
C, H	Pyrolysis
Benzo-α-pyrene	Chromatograph, Fluorescence
Trace Metals	Emission Spectroscopy, Atomic Absorption
Aldehydes	Polarography
NH_3	Steam Distillation, Titration

1. Fuels

Each test fuel was analyzed to verify concentrations of additives under study. Additionally, complete physical analysis were determined on the base stock test fuel. These analysis include (distillation, octane numbers, fluorescence indicating analysis FIA composition, and Reid vapor pressure [RVP] and trace metal).

2. Oils

Engine oils were examined for trace metals both before and after test runs. Compliance of physical properties with specifications was verified. The oils were only checked on the engine stand runs, not on vehicles.

3. Diluent Air

Mass and composition of the filtered diluent air particulate was determined with the engine or vehicle operating in the air pick-up zone as during a test run. This data was necessary to provide a correction factor applicable to the mass emission rates determined during a test run.

4. Exhaust Gases

Engine exhaust gases were analyzed routinely several times during the conditioning sequence and during sampling runs. Schematically, exhaust gas sample points are as shown earlier in Figure 1. The engine exhaust gas was analyzed for oxygen, nitrogen, carbon monoxide, carbon dioxide, and total unburned hydrocarbons. The hydrocarbons were broken down into saturates and unsaturates. These analyses were done by gas chromatography, chemical absorption, and a total hydrocarbon analyzer. Data reduction was via an IBM 1800 computer through a Bell Telephone ASR 33 Teletype interface.

a) Analytical Equipment

A Fisher Gas Partitioner was used for the analysis of oxygen, nitrogen, carbon monoxide, and carbon dioxide. The partition column consisted of a 6-foot section containing hexamethyl phosphoramide and a 6-1/2 foot section containing 13x molecular sieves in series.

Total hydrocarbons were obtained from a Beckman Model 109A Total Hydrocarbon Analyzer. The concentration of unsaturated hydrocarbons was determined by passing the sample through an absorption tube (1/2" x 8") filled with 30-60 mesh pink Chromosorb impregnated with 50 percent mercuric perchlorate.

The output of the gas chromatograph was coupled with a Hewlett-Packard Model 3370A Digital Intergrator which has an ASCII coded output to drive an ASR 33 Teletype and punch paper tape.

b) Sampling

A Neptune Dyna-Pump was used to pull the sample from the exhaust pipe sampling point through 1/4" OD stainless steel tubing and transfer it to the total hydrocarbon analyzer and the gas sampling valve of the gas chromatograph through 1/8" OD stainless steel tubing. A manifold system was provided to allow the operator to calibrate the equipment with the appropriate standards.

c) Standardization

A gas mixture containing known concentrations of oxygen, nitrogen, argon, carbon monoxide, carbon dioxide, and n-hexane was used as a reference standard for the total hydrocarbon analyzer and the Fisher Gas Partitioner.

d) Operation

The operator typed the proper computer code and program number on the teletypewriter, injected the reference standard, and pressed the integrator start button. As the peaks emerged, the time and area information was encoded and stored on punched paper tape. Each succeeding exhaust gas was identified along with the total hydrocarbon level, and run in the same manner as the standard. When the series was finished, the punched tape was sent to the computer by teletype over regular telephone lines.

e) Data Reduction

A typical output format for the gas analysis is shown in Figure 2. Identification of the components in the standard was based upon each peak size in descending order. Estimated retention time was the updated time of each peak in the standard. Retention time windows are 4 seconds plus 2 percent of the retention time. Actual percent is a direct ratio of the area counts in the unknown sample to the area counts in the standard times the volume percent in the standard. The total percent actual will normally be 97-98 percent since water is removed from the saturated sample after the sampling valve.

A correction for the unresolved argon in oxygen was made based upon response factors and the amount of argon found in a number of exhaust gas samples by mass spectroscopy.

The actual percent was normalized to 100 percent in the next column on a moisture free basis, and an Exhaust Gas Analysis report was issued (Figure 2). The air-to-fuel ratio was calculated from this analysis, the total hydrocarbon content, and the percent carbon in the fuel.

5. Oxides of Nitrogen

a) Equipment

Beckman Ultraviolet Analyzer
Beckman Infrared Analyzer
Recorder - Texas Instrument Company

The above pieces of equipment were in a single, self-contained unit built by Scott Research Labs Inc., San Bernardino, California.

Figure 2

```
G. C. ANALYSIS - TECHNICAL DATA -                  10-16-70
GOV RUN 23 OCT 16
CYCLE 2 72.9 HOURS
HC 620.

 PEAK     TIME          PCT. VOL.        COMPOUND
  NO.  ACT.    EST.   ACTUAL   NORM.   IDENTIFICATION


   1    22.     21.    0.000    0.000  COMPOSITE
   2    59.     59.   12.003   12.366  CARBON DIOXIDE
   3    83.     83.    1.493    1.538  OXYGEN
                       0.900    0.927  ARGON
   4   104.    107.   81.038   83.492  NITROGEN
   5   187.    188.    1.626    1.675  CARBON MONOXIDE
                     -------  -------
                      97.060  100.000  TOTALS
                       2.940           BALANCE BY DIFFERENCE
                       2.940           TOTAL CONTAMINATION LEVEL

-------------------------------------------------------------
-------------------------------------------------------------

        EXHAUST GAS ANALYSIS         10-16-70

GOV RUN 23 OCT 16
CYCLE 2 72.9 HOURS
HC 620.

 TIME  PERCENT  IDENTIFICATION

  83.     0.9  ARGON
 107.    83.5  NITROGEN
  83.     1.5  OXYGEN
 108.     1.68 CARBON MONOXIDE
  59.    12.4  CARBON DIOXIDE
        -----
        100.0  TOTAL

FRACTION CARBON IN FUEL 0.8625

TOTAL HYDROCARBON CONTENT  620. PPM.

AIR/FUEL RATIO 14.8
```

b) Calibrating Gases

Nitric oxide (3545 ppm in nitrogen)
Nitrogen dioxide (862 ppm in nitrogen)

These standard gases were purchased from Scott Research Labs, Inc.

Nitrogen was used as zero calibrating gas.

c) Procedure

Before making NO, NO_2 measurements, the paper filters (Whatman #3) to each analyzer were changed and the Drierite dryer in the exhaust sample line was replaced. Both analyzers were standardized using the appropriate calibrating gas at a constant flow. The zero standardizing was done using nitrogen as the calibrating gas and using the same flow rate.

After the instrument was standardized, the exhaust gas was passed through the analyzer using the same flow rate as in the standardization step. The NO, NO_2 values were recorded by the dual pen Servo-riter recorder. Figure 1 indicates the source of the exhaust gas sample.

6. Exhaust Particles

The collection and classification techniques employed allow the calculation of mass emission rates in grams/mile of exhaust particulate. Additionally, cumulative mass distribution data can be calculated. Several collection methods were used, and have been discussed previously in Section III-B. The specific techniques for chemical analysis of this particulate matter are discussed in this section.

a) Carbon and Hydrogen

The percentage of carbon and hydrogen in the particulate was determined by pyrolysis and collection of the combustion products. An entire 142 mm glass fiber filter containing the particulate was placed in a large platinum boat. The boat was then transferred to a combustion tube, and the sample was combusted at 1100°C for 3/4 hour. Carbon dioxide and water were absorbed in micro absorption tubes and weighed in the conventional manner. The C and H values were then calculated from the increase in weight using the given weight of the particulate.

In general, this technique is quite accurate for carbon and hydrogen analysis. However, the small sample sizes generated in a 23 minute cycle or from vehicles or engines operating on unleaded fuel make it difficult to obtain precise results. For example, the 142 MM Gelman glass fiber filters have a blank of approximately 7 mg for hydrogen and a spread of nearly 1 mg. For carbon the blanks are over 2 mg with a spread of 0.5 mg. It is not uncommon to have sample sizes of less than 2 mg; therefore, the inherent inaccuracy of weighings (even using a 5 place balance) plus the large blank size make the results of a small sample only meaningful in a gross comparative sense.

This technique can be used on samples collected on the Andersen Sampler plates by careful transfer of the particulate to the combustion chamber. However, even with the best handling techniques the transfer of particulate is only about 30 percent. In general, engine runs in which very little sample was collected on the filter pads also gave very little on the Andersen Sampler Plates.

Nitrogen can also be determined by pyrolysis, but due to the small sample size no meaningful results have been obtained on nitrogen content.

b) Benzo(α)pyrene

Samples of exhaust particulate were collected on Gelman 142 mm glass fiber filter pads in a Millipore filter holder operating at 1 cfm. Particulate weights gathered in this fashion ranged from 0.2 to 35 mg. The samples on the glass filter pads were analyzed for benzo(α)pyrene in the following manner.

When available a sample of at least 10 mg (on either one or two filter papers) was used for analysis. The filters were folded and rolled with the particulates toward the inside of the roll and tied with copper wire. The rolls were Soxhlet extracted for at least 6 hours (with siphoning four to six times per hour) with 75 ml of benzene. The extracts were evaporated under a stream of filtered air at room temperature to approximately 3 ml. This concentrate was filtered through a M-fritted glass filter into a tared vial. The flask and filter were washed three times with approximately 2 ml of benzene for each wash. The combined filtrates were evaporated to dryness at room temperature with a stream of filtered air.

The residues obtained from both sample and blank filters were weighed and the difference between them designated "benzene soluble weight" for each sample. The residue was dissolved in 0.2 ml of methylene chloride and a 10-40 μl aliquot was spotted in 2 μl increments on a pre-conditioned Alumina TLC plate along with a known standard of benzo(α)-pyrene in methylene chloride. The TLC plates were conditioned by heating at 120°C for 1.5 hours and desiccating overnight in a 45 percent relative humidity chamber (saturated aqueous zinc nitrate). The TLC plate was developed in an unsaturated tank containing 20 ml of ethyl ether in 200 ml of n-pentane to a height of 15 cm (approximately 45 minutes).

The benzo(α)pyrene spots were identified by comparison of R_f's with that of the standard spot under an ultraviolet lamp. The spots, marked with a pencil, were circumscribed with a #15 cork borer and scraped from the plate into vials. All TLC work was performed as much as possible in a dimly lighted area to avoid decomposition of the benzo(α)pyrene.

Five ml of 5 percent acetone in n-pentane was added to the alumina in the vial and it was agitated for 15 minutes on a mechanical shaker. The slurry was filtered through a F sintered glass filter into a vial, washing the alumina four times with approximately 2 ml of 5 percent acetone in n-pentane with a 45-second soak period between each wash. The combined filtrates were evaporated to dryness at room temperature using a stream of filtered air. The benzo(α)-pyrene residue was taken up in 2.0 ml of concentrated sulfuric acid. This solution was evacuated for five minutes to remove trapped air bubbles and its fluorescence was measured in a one-cm cell at 540 nm while exciting at 470 nm on an Amino-Bowman Spectrophotofluorometer using a #4 slit arrangement and a sensitivity of 30.

Standard and blanks were carried through the entire TLC procedure. The blanks were subtracted from all fluorescence readings and the net fluorescence values for each sample were used to calculate the amount of benzo(α)pyrene present. Throughout all steps in the procedure the samples were refrigerated when not actually being processed and exposure of the samples to light was kept at a minimum.

c) Trace Metals

Both atomic absorption and emission spectrometry were used for determination of metals in the particulate. Atomic absorption was primarily used for lead determination. Trace metals were determined by ES on millipore filters while lead was determined as a percent of the particulate collected on the 142 mm, 1 cfm fiberglass filter.

1) Emission Spectrometry

a. Principle

Organic matter in the sample is destroyed by wet ashing in sulfuric, nitric and perchloric acids. The resulting solution is taken to dryness and the residue is taken up in a spectroscopic buffer solution containing the internal reference element, palladium. A portion of the solution is dried on pure graphite electrodes. The electrodes thus prepared are excited in an a.c. arc discharge and the spectrum is photographed. The intensity ratios of selected lines are determined photometrically and the concentration of each element is read from an analytical curve relating intensity ratio to concentration.

b. Apparatus

1) Excitation. Excitation is obtained by the use of a 2400 volt a.c. arc discharge - Jarrel-Ash Custom Varisource, or equivalent.

2) Spectrograph - Baird 3 meter grating spectrograph. Reciprocal dispersion is 5.55 A/mm in the first order.

3) Developing equipment - Jarrel-Ash Company. Plates are developed in a thermostatically controlled developing machine, washed and dried over heat in a stream of air.

4) Densitometer. Spectral lines are measured with a non-recording projection type densitometer. Densitometer Comparator, Baird Associates Inc., or equivalent.

5) Calculating equipment. A calculating board is employed to covert densitometer readings to log intensity ratios. Jarrel-Ash Co.

6) Wet ashing equipment. A micro Kjeldahl digestion rack is used for wet ashing the organic solvents.

c. Reagents and Materials

1) Distilled nitric and perchloric acids. Perchloric acid is an intense oxidizing agent. Organic matter should not be heated in perchloric acid unless in the presence of sulfuric or nitric acid.

2) Sodium nitrate, reagent grade ($NaNO_3$).

3) Palladium diamine nitrite, $Pd(NH_3)_2(NO_2)_2$.

4) Water soluble salts of the elements Al, Ca, Cu, Fe, Mg, Mn, Ni, Pb, Sn, and Zn.

5) Electrodes, high purity graphite, 1/4" diameter by 3/4" length. Ultra Carbon Corporation.

6) Photographic plates - Eastman Spectrum Analysis No. 3.

7) Kjeldahl flasks, 10 ml.

d. Calibration

1) 0.2182 gm of palladium diamine nitrite $Pd(NH_3)_2NO_2)_2$ were dissolved in water. 10 ml of concentrated reagent grade nitric acid were added and the mixture diluted to volume with water in a 100 ml volumetric flask. This solution contains 1 mg Pd per ml.

2) A buffer solution was prepared by dissolving 20 gm of sodium nitrate in water. 5.0 ml of the palladium solution above and 7.5 ml of concentrated reagent grade nitric acid were added and the whole diluted to 100 ml.

3) A stock solution containing 0.01% (0.1 mg/ml) each of the elements Al, Ca, Cu, Fe, Mg, Mn, Ni, Pb, Sn, and Zn was prepared. Two aliquots of this solution were diluted ten-fold and one hundred-fold to provide 0.001% and 0.0001% solutions.

4) Standard additions of the impurity elements were made to Kjeldahl flasks as shown in Table 6.

5) 0.5 ml of concentrated reagent grade sulfuric acid was added to the Kjeldahl flasks and the solution evaporated to dryness. After cooling, 1 ml of concentrated nitric acid was added and the mixture was evaporated to dryness again. The residue was taken up in 5 ml of buffer solution, warming, if necessary, to put the salts into solution.

6) The end of the 3/4" graphite electrodes was polished on filter paper and placed in a stainless steel drying tray. A drop of kerosene was placed on the top of each electrode to seal the porosity and the electrode allowed to dry. One pair of electrodes was prepared for each of the standard addition solutions by pipetting 0.03 ml of the solution onto the end of each electrode. The electrodes were dried slowly over micro burners in a gas drying oven and stored in a desiccator until run.

7) The samples were excited in water cooled electrode holders using the following conditions:

(1) Current, 4.0 amps, a.c. arc.
(2) Spectral region, 2150-3550 A.
(3) Slit width, 50μ.
(4) Electrode gap, 2 mm.
(5) Pre-burn period, 10 seconds.
(6) Exposure period, 90 seconds.

Table 6

Concentration	ml. of standard addition impurity solution		
Blank			
0.00001%	0.5 ml.	0.0001%	solution
0.000025%	1.25 ml.	"	"
0.00005%	0.25 ml.	0.001%	"
0.0001%	0.5 ml.	"	"
0.00025%	1.25 ml.	"	"
0.0005%	2.5 ml.	"	"
0.00075%	0.375 ml.	0.01%	"
0.001%	0.5 ml.	"	"
0.0025%	1.25 ml.	"	"
0.005%	2.5 ml.	"	"
0.01 %	5.0	"	"

Table 7

Analytical Line Pairs

Element	Analytical Line A	Internal Standard Line A	Concentration Range %
Al	3092.71	3027.91 Pd	0.000025-0.0010
Ca	3179.33	"	0.00025-0.010
Cu	3273.96	"	0.00001-0.00025
Fe	3021.07	"	0.0001-0.010
Fe	3020.64	"	0.000025-0.0050
Mg	2802.69	"	0.000025-0.0010
Mg	2779.83	"	0.0005-0.010
Mn	2933.06	"	0.0005-0.010
Mn	2794.82	"	0.00001-0.0010
Ni	3414.77	"	0.000025-0.0010
Ni	3037.94	"	0.0005-0.010
Pb	2873.32	"	0.0010-0.010
Pb	2833.07	"	0.00005-0.0050
Sn	3175.02	"	0.00005-0.0050
Sn	2863.33	"	0.00075-0.010
Zn	3345.02	Background	0.0001-0.010

8) The emulsion was calibrated by use of a stepped filter or by other recommended methods described in the "Recommended Practice of Photographic Photometry in Spectrochemical Analysis" A.S.T.M. Designation: E116, Methods for Emission Spectrochemical Analysis, (1964).

9) The emulsion was processed according to the following conditions:

(1) Developer (D19, 20.5°C), 3 1/2 minutes.
(2) Stop bath (SB-4), 1 minute.
(3) Fixing bath (Kodak Rapid Fixer), 2 minutes.
(4) Washing, 3 minutes.
(5) Drying, in a stream of warm air.

10) The relevant analytical line pairs were selected from Table 7. The relative transmittances of the internal standard line and each analytical line were measured with a densitometer. The transmittance measurements of the analytical line pairs were converted to intensity ratios by the use of an emulsion calibration curve and a calculating board.

11) Analytical curves were constructed by plotting concentration as a function of intensity ratio on log-log graph paper. For best results, the average of at least four determinations recorded on two plates were plotted.

e. Procedure

1) The available sample was weighed directly into a Kjeldahl flask. Sulfuric acid was not used in the wet ash procedure because test samples usually contained

a large amount of lead which would form the insoluble sulfate. Wet oxidation was carried out with nitric and perchloric acid only. Extreme caution was exercised in the use of this technique. Concentrated nitric acid was added dropwise, a few tenths ml at a time, to the hot mixture to aid in oxidation. A few drops of concentrated perchloric acid may be added to the hot solution after most of the free carbon has been destroyed, to hasten complete oxidation. When the solution became water clear, it was evaporated to dryness. After cooling, 0.5 ml of nitric acid was added and the mixture evaporated to dryness. The addition of 0.5 ml of nitric acid was repeated and the solution evaporated to dryness again. The inorganic residue was dissolved in dilute nitric acid and the volume adjusted to a known concentration, usually 10 mg/ml. If the original sample size was below 30 mg, a less concentrated solution was usually made up. Aliquots of this solution were taken to dryness and then the buffer solution (d2) added in an amount to give a dilution factor of 100x. One sample was analyzed by the direct reader while a second was examined photographically. Some samples had to be run at factors larger than 100x in order to get the concentration for some elements to fall within the range of the analytical curves. By varying the sample to buffer ratio any number of concentration or dilution factors could be achieved. A blank of the acids used was carried through in the same manner as the sample.

2) Proceed as in d(6), (7), (8), (9), and (10) of the calibration procedure. Duplicate spectra were recorded for each sample.

f. Calculations

The intensity ratios were converted to concentration by use of the analytical curves.

g. Precision and Accuracy

Representative precision and accuracy of the method are given in Table 8. Each of the twelve samples A_1, A_2, A_3, B_1, B_2, B_3, C_1, C_2, C_3, D_1, D_2, D_3, was analyzed by means of duplicate excitation.

2) Atomic Absorption

a. Method for Lead Determination

Following nitric acid digestion, particulate samples were washed into 50-ml volumetric flasks and diluted to mark. This normally put the concentration of lead in the flasks between 20 and 200 µg Pb/ml. If the concentration was higher than 200 µg Pb/ml, the sample required redilution. The samples were analyzed on an atomic absorption spectrophotometer (Perkin-Elmer Model 303) using a hollow cathode lamp with a lead cathode filament. Operating conditions were as follows: 10 milliamps tube current, light path slit opening - 4, ultraviolet light range, acetylene-air oxidizing flame, one-slot burner head, wavelength - 2170 angstroms. The sample solution is aspirated into the flame where lead atoms present absorb the light from the lead cathode filament. The amount of absorbed light is proportional to the concentration of lead. The samples were analyzed in conjunction with the following series of lead standards: 10, 20, 40, 60, 80, 100, 150, and 200 µg Pb/ml. The concentration of the standards was plotted versus their absorbance values giving a standard curve. With the absorbance values for the samples and the standard curve, it was possible to determine the concentration of

TABLE 8

REPRESENTATIVE PRECISION AND ACCURACY OF EMISSION SPECTROSCOPY

Sample	% Al	% Ca	% Cu	% Fe	% Mg	% Mn	% Ni	% Pb	% Sn	%Zn
A_1	0.000044	0.00043	0.000048	0.00043	0.00049	0.00046	0.00047	0.00056	0.00052	0.00040
	0.000052	0.00050	0.000054	0.00055	0.00052	0.00057	0.00055	0.00059	0.00059	0.00045
A_2	0.000045	0.00043	0.000046	0.00044	0.00047	0.00051	0.00045	0.00050	0.00053	0.00054
	0.000052	0.00037	0.000047	0.00043	0.00050	0.00050	0.00051	0.00051	0.00050	0.00040
A_3	0.00004	0.00043	0.000050	0.00046	0.00053	0.00049	0.00047	0.00052	0.00050	0.00052
	0.000052	0.00050	0.000048	0.00046	0.00049	0.00046	0.00048	0.00053	0.00046	0.00042
B_1	0.00012	0.00105	0.00012	0.0010	0.00105	0.0010	0.0010	0.00105	0.0011	0.00094
	0.000097	0.00093	0.00010	0.00094	0.00095	0.0012	0.00096	0.00098	0.00094	0.0012
B_2	0.000097	0.00086	0.000099	0.00090	0.00092	0.0011	0.0010	0.0010	0.00105	0.00125
	0.000094	0.00088	0.000095	0.00105	0.00091	0.00066	0.00105	0.00105	0.00105	0.0010
B_3	0.000082	0.00085	0.000095	0.0010	0.0010	0.00086	0.0010	0.0010	0.00099	0.00096
	0.00011	0.00074	0.000096	0.0010	0.00090	0.00092	0.00105	0.0010	0.0010	0.00115
C_1	0.00028	0.0023	0.00023	0.0025	0.0023	0.00265	0.00245	0.00235	0.00255	0.0014
	0.00030	0.0018	0.00028	0.0030	0.0023	0.00195	0.00265	0.00255	0.0027	0.00215
C_2	0.00020	0.00225	0.00023	0.0023	0.0023	0.00265	0.0023	0.00245	0.00215	0.00225
	0.00023	0.00223	0.00025	0.00235	0.0024	0.00275	0.00245	0.0026	0.0023	0.0030
C_3	0.00024	0.0025	0.00026	0.00275	0.0023	0.00245	0.0026	0.0025	0.0025	0.0030
	0.00028	0.00275	0.00028	0.00285	0.0024	0.0025	0.00255	0.00245	0.00265	0.0020
D_1	0.00074	0.0070	--	0.0055	0.0057	0.0059	0.0055	0.0056	0.0064	0.0058
	0.00064	0.0064	--	0.0053	0.0051	0.0058	0.0058	0.0045	0.0059	0.0050
D_2	0.00059	0.0049	--	0.0057	0.0048	0.0045	0.0056	0.0045	0.0053	0.0050
	0.00063	0.0057	--	0.0059	0.0047	0.0048	0.0057	0.0048	0.0057	0.0060
D_3	0.00059	0.0043	--	0.0050	0.0045	0.0047	0.0050	0.0043	0.0054	0.0037
	0.00053	0.0030	--	0.0055	0.0055	0.0054	0.0055	0.0049	0.0049	0.0041

A_1, A_2, and A_3 contain 0.00005% of Al and Cu, and 0.0005% of each other element. B_1, B_2, and B_3 contain 0.0001% of Al and Cu, and 0.0010% of each other element. C_1, C_2, and C_3 contain 0.00025% of Al and Cu and 0.0025% of each other element. D_1, D_2 and D_3 contain 0.0005% of Al and Cu and 0.0050% of each other element.

lead in the samples. The sensitivity for the lead determination in an air-acetylene flame is about 0.25 μg Pb/ml at 1 percent absorption. The detection limit is 0.1 μg Pb/ml.

b. Determination of Lead and Iron in Engine Combustion Chamber Deposits

These samples were thoroughly ground in a mortar prior to analysis to obtain uniform samples. The ground sample was dissolved in nitric acid and lead determined by atomic absorption. A portion of the sample solution was also used in the determination of iron. Iron is reduced with hydroxylamine to the ferrous state, and reacted with 1,10-phenanthroline in an acetate buffered solution (pH 5) to form an orange-red complex. Photometric measurements were made using a Beckman DU-2 spectrophotometer. Operating conditions were as follows: sensitivity setting - 2, slit opening - 0.10 mm, wavelength - 510 nm, 40 mm optical cells. The concentration of iron was determined from a standard curve. For a one gram sample diluted to 100 ml, the detection limit is about 1 ppm and the sensitivity ± 1 ppm.

c. Gravimetric Method for Lead Determination in Millipore Filters

Following nitric acid digestion, concentrated sulfuric acid was added to the sample to precipitate lead sulfate. The solution was filtered, and the precipitate dried and weighed to determine the amount of lead percent. In addition, the filtrate was analyzed by atomic absorption for trace amounts of lead. This analysis is included in the total amount of lead reported for the sample.

d. Determination of Lead and Other Metals in Fiberglass Filters

The fiberglass filters cannot be digested completely with nitric acid. They were cooked with concentrated nitric acid for two hours to leach out the metals. The pulp was filtered and washed and the filtrate analyzed by atomic absorption for lead, and by emission spectroscopy for other metals.

7. Condensate Analyses

Condensate was collected from the raw exhaust as described in Section III-C. The condensate was analyzed for aldehydes and NH_3 using the procedures outlined below.

a) Aldehydes

The analytical method for the determination of carbonyl compounds in automotive exhaust emissions employed polarographic techniques. Samples for analysis were collected from undiluted exhaust effluent using ice-water cooled cold traps and via a sample probe welded into the engine or vehicle exhaust system. A Princeton Applied Research Model 170 Electrochemistry System was used as the monitoring device. The derivative pulse polarographic mode yielded the best combination of resolution and sensitivity for the classification of carbonyl compounds. A dropping mercury electrode with a Princeton Model 172 Drop Timer was employed as the working electrode.

Hydrazine derivatives (hydrazones) were employed for the determination of the carbonyl compounds, since hydrazones are easier to reduce than the free compounds, thus eliminating many possible interferences.

An acetate buffer of approximately pH 4 (an equimolar mixture of acetic acid and sodium acetate, 0.1M in water) was used to control pH for hydrazone formation and also acted as supporting electrolyte. Hydrazine was added as a 2 percent aqueous solution. In this system formaldehyde gave a peak potential (half-wave potential) of -0.92v vs. a saturated calomel reference electrode. A platinum wire was employed as the auxiliary electrode.

With the above system, it is possible to distinguish between and simultaneously determine aromatic aldehydes, formaldehyde, higher aliphatic aldehydes, and aliphatic ketones as shown in Figure 3.

Since aromatic ketones, e.g. benzophenone, give polarographic response in pH 4 buffer without hydrazine, it is also possible to detect aromatic ketones. Lead and zinc could also be determined from the samples under these conditions.

Since formaldehyde was the main carbonyl component of the condensate samples, all results were calibrated against and reported as formaldehyde. The upper curve in Figure 4 shows an actual sample without hydrazine present and demonstrates the lack of interference in the carbonyl region. The lower curve shows the same sample after the addition of hydrazine. Figure 5 shows the same solution after the addition of a formaldehyde standard. These two figures clearly establish the presence of formaldehyde in the exhaust samples.

Procedure

Pipet 2 ml of methanol sample into a 25-ml volumetric flask. Add 10 ml of pH 4 acetate buffer and dilute to volume with water. Transfer this solution to a polarographic cell and deaerate with oxygen-free nitrogen for ten minutes. Record a

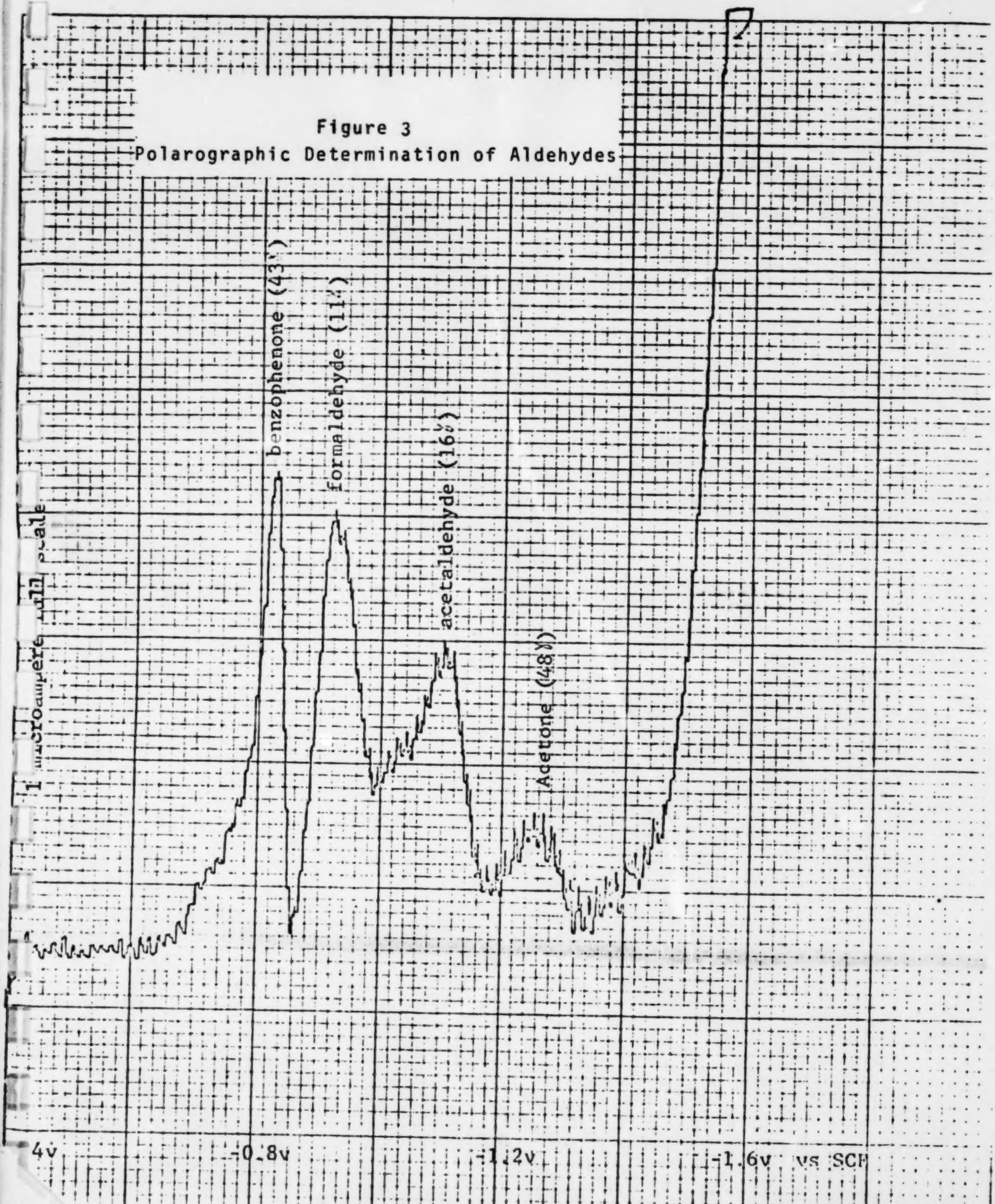


Figure 3
Polarographic Determination of Aldehydes

Figure 4
Polarographic Determination of Aldehydes

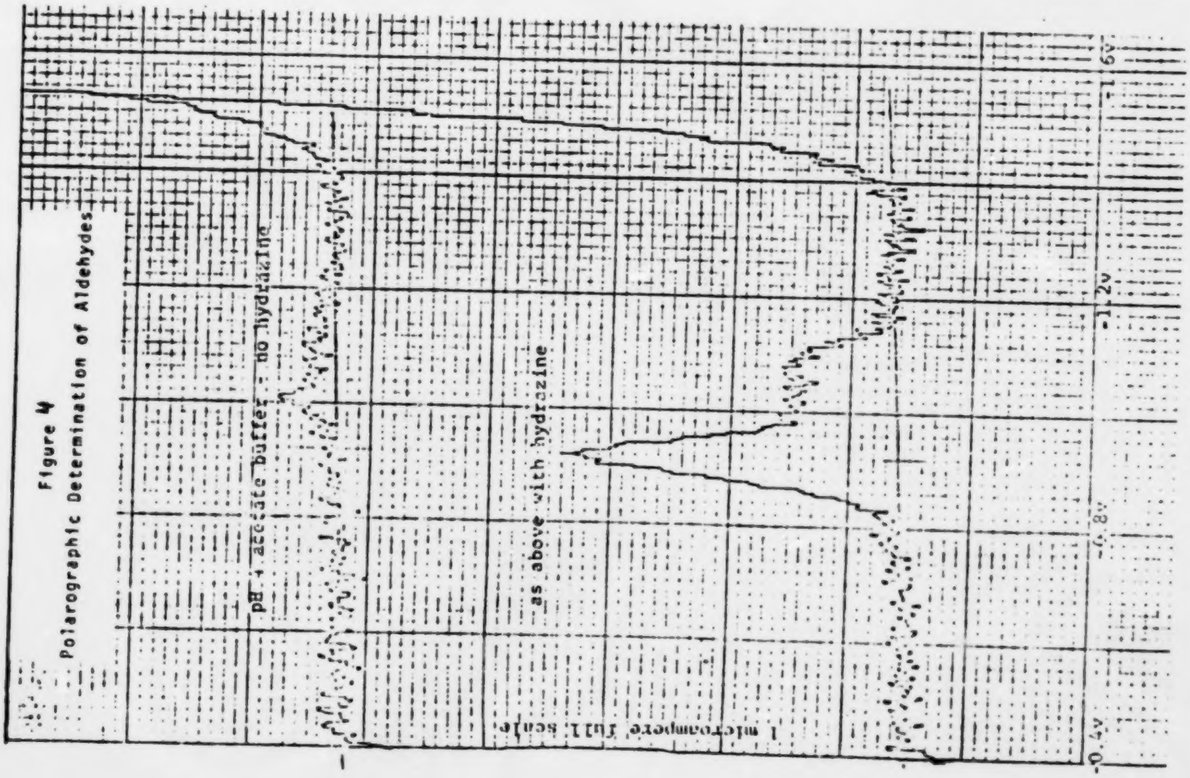
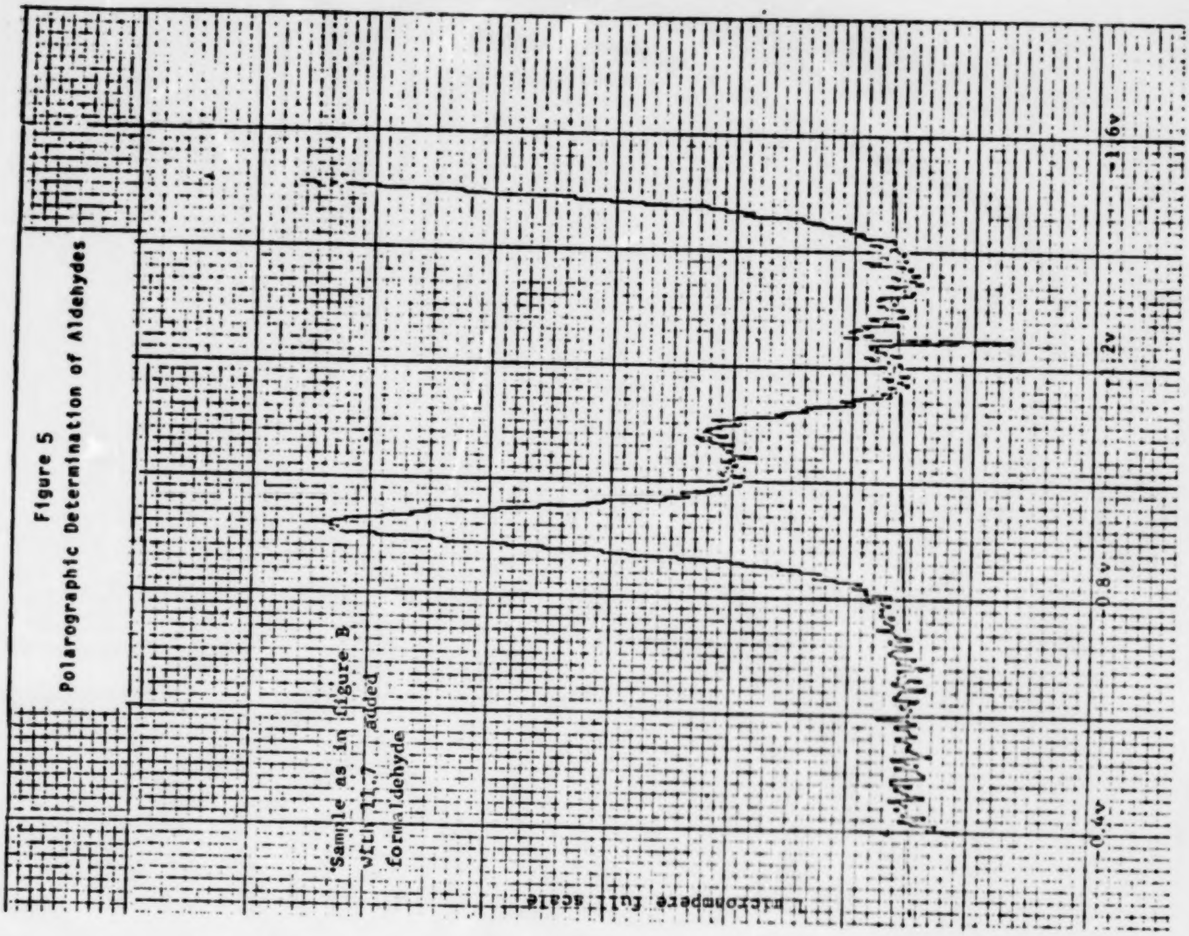


Figure 5
Polarographic Determination of Aldehydes



derivative pulse polarogram from 0 to -1.6 V vs. SCE. Add 2 ml of hydrazine reagent to the polarographic cell and deaerate for 5 minutes. Again, record the polarogram from 0 to 1.6 V vs. SCE.

Lead and aromatic ketones are determined from the waves obtained without hydrazine at the peak potentials listed above. Formaldehyde, higher aliphatic aldehydes, aromatic aldehydes, and aliphatic ketones can be determined from the second polarogram with hydrazine present.

All responses should be calibrated by addition of known amounts of standard compounds to actual runs. Peak heights are linear with concentration.

In this system, zinc has a peak potential of -1.00 V vs. SCE, but it can be differentiated from benzophenone by the fact that it possesses only one polarographic wave.

A blind comparison of the polarographic technique vs. the MBTH technique was made, and the results were as follows, expressed as formaldehyde:

MBTH	Polarographic
340 ppm	300 ppm
1500 ppm	1530 ppm
430 ppm	480 ppm
105 ppm	110 ppm
150 ppm	110 ppm

b) Ammonia

Ammonia is present in the exhaust gas condensate and is analyzed in the following manner.

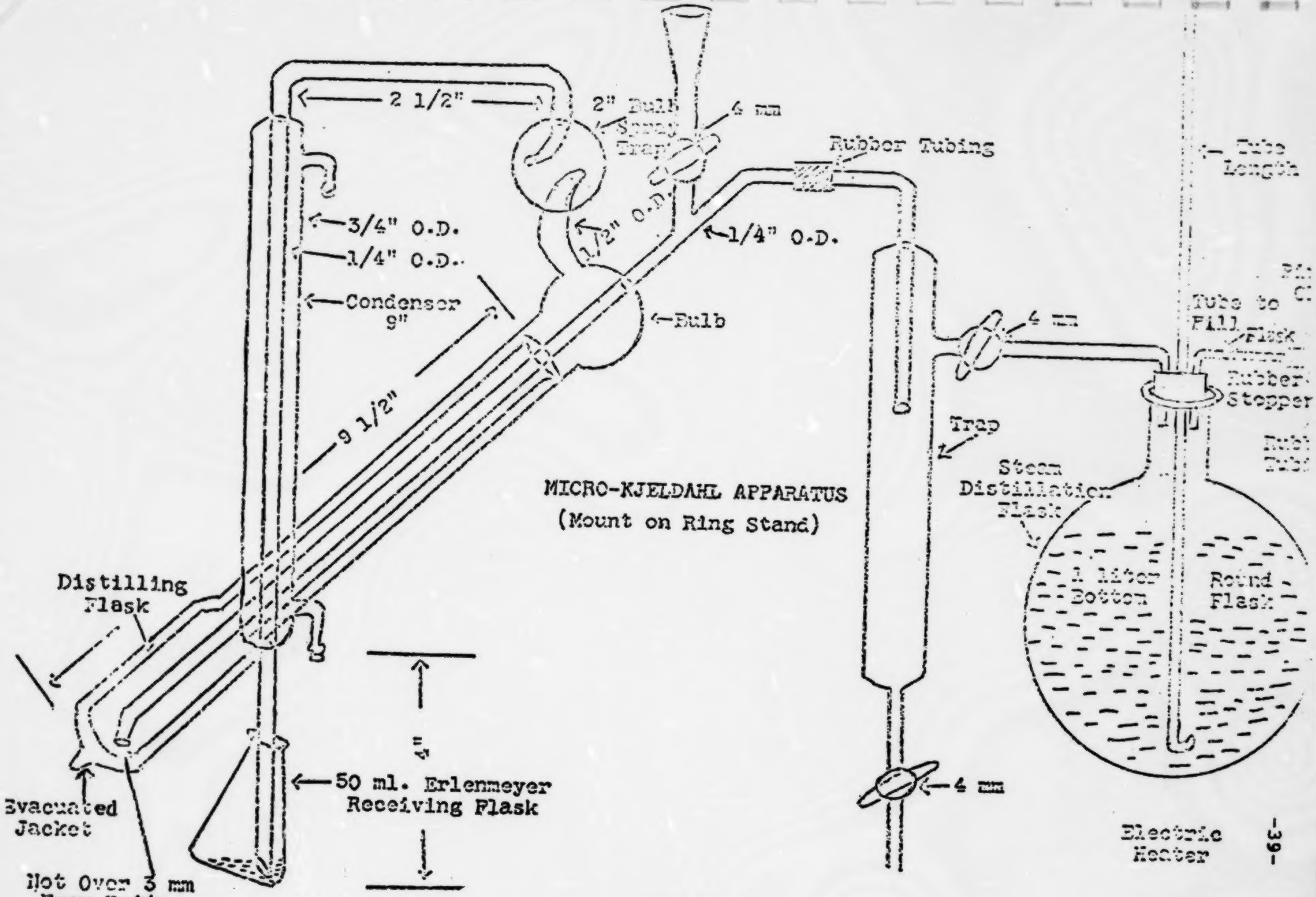

2 1/2"
2" Bulb Spray Trap
4 mm
Rubber Tubing
Tube Length
3/4" O.D.
1/4" O.D.
1/2" O.D.
1/4" O.D.
Condenser 9"
Bulb
9 1/2"
Tube to Fill Flask
4 mm
Rubber Stopper
Trap
Steam Distillation Flask
1 Liter Round Bottom Flask
MICRO-KJELDAHL APPARATUS
(Mount on Ring Stand)
Distilling Flask
Evacuated Jacket
Not Over 3 mm From Bottom
4"
50 ml. Erlenmeyer Receiving Flask
4 mm
Electric Heater

FIGURE 6

APPARATUS FOR DETERMINATIONOF NH_3

A 5-10 cc aliquot of condensate is added to a 50 percent potassium hydroxide solution. This mixture is then steam distilled into an excess of 0.010 N hydrochloric acid. The excess acid is determined by adding potassium iodide and iodate and titrating the liberated iodine with 0.010 N sodium thiosulfate.

This technique is capable of determining ammonia as low as 0.3 ppm. Figure 6 is a sketch of the apparatus used for the determination.

The analytical procedures given herein have been adapted from literature sources or developed upon the basis of experimental data which are believed to be reliable. In the hands of a qualified analyst they are expected to yield results of sufficient accuracy for their intended purposes. However, The Dow Chemical Company makes no representation or warranty whatsoever concerning the procedures or results to be obtained and assumes no liability in connection with their use. Users are cautioned to confirm the suitability of the methods by appropriate tests.

IV. EXPERIMENTAL RESULTS

The current extention to contract EHS 70-101 was outlined into five basic tasks. These tasks are presented in Table 9 with a brief description of the objective of each task and the approach used to accomplish the objective.

TABLE 9
TASKS AND OBJECTIVES

TASK I - Evaluation of Particulate Sampling Parameters

Objective: To evaluate the relative significance of various sampling parameters on the collection of particulate matter and to identify therefrom a set of sampling conditions which will afford reliable and meaningful data for the remainder of the work program.

Approach: Particulate matter from air diluted automotive exhaust was sampled and the effect of changes in the following sampling variables was monitored: sample line temperature, dilution ratio, sample probe location, filter flow rate, and sampling time. This work was performed using non-leaded fuel. Grams/mile of particulate was measured.

TASK II - Determination of Baseline Data from Engine Dynamometer Tests

Objective: To establish baseline data for particulate emissions, aldehydes, ammonia and benzo-α-pyrene present in the exhaust effluent of an internal combustion engine operating on non-leaded and low-lead gasoline under controlled conditions on an engine dynamometer.

Approach: A 1972 Pontiac 400 CID V-8 engine was procured and a reference set of tests were run on this engine using non-lead and low-lead fuels. The above emission data was generated under the following test conditions:

Road load 60 mph
Road load 30 mph
Mild cycling (Dow cycle) to include cold start

For each of these conditions, the effect of the following variables on such emissions were evaluated.

Air/fuel ratio (three different values at road load 30 and 60, 1 value under cycling)
Ignition timing (two different settings)

TASK III - Evaluation of Emission Control Devices by Engine Dynamometer Tests

Objective: To evaluate the effect of various exhaust emission control devices on the non-regulated emissions identified in Task II.

Approach: For each emission control device to be considered the tests outlined in Task II were repeated as applicable. The devices tested included:

Sub-task IIIA	Three HC-Co oxidation catalysts
Sub-task IIIB	One NO_x reduction catalyst
Sub-task IIIC	Exhaust gas recirculation

TASK IV - Evaluation of the Effect of Emission Control Devices on Non-Regulated Emissions by Vehicle Testing

Objective: To characterize the non-regulated emissions outlined in Task II for vehicles equipped with emission control devices.

Approach: Vehicles equipped with emission control devices were tested periodically (as a function of mileage accumulation) and the above non-regulated emissions measured using the 1975-76 Federal Test Procedure on a chassis dynamometer. Four of these vehicles were made available from automotive company durability programs. Where possible, each vehicle was tested on at least three separate occasions. Additional vehicles equipped by the Office of Air Programs, Environmental Protection Agency (EPA), were tested as scheduled by the Contract Officer.

TASK V - Diesel Engine Characterization

Objective: To initiate a limited diesel engine study to establish baseline data for emissions present in the exhaust stream.

Approach: A single cylinder Labeco diesel engine was used to study sampling parameters and the effect of a dilution tube on the diesel exhaust.

The data and conclusions for each task are presented separately, as well as any discussion of operating parameters, analyses, or effects of devices.

A. TASK I

1. Introduction

The major objective of the first task outlined in the current extension to the subject contract was to study the effect of specific engine variables on certain non-regulated exhaust emissions under highly controlled conditions. The emissions defined for study included particulate matter (organic and inorganic), aldehydes, ammonia and benzo-α-pyrene. Studies were made on engines operating on non-leaded and low-lead fuels.

During the course of some preliminary studies undertaken in our previous years work, alarming differences were noted when particulate matter emitted in the exhaust stream of an engine operating on non-leaded gasoline was collected on filters operating at different flow rates and temperatures.

In order to reach an understanding of the above effects and to allow the definition of a meaningful set of particulate sampling parameters which could be used throughout the current contract efforts, a study had been made of a number of sampling variables and their effect on the mass of particulate matter collected at a filter.

2. Experimental Procedure

All of the studies described herein were conducted using either a 1971 Chevrolet Impala fitted with a 350 CID V-8 engine and operated on a Clayton Model chassis dynamometer, or a 1972 Pontiac 400 CID V-8 engine operated on a General Electric Model dynamometer. Both the vehicle and the engine were run on Indolene 0 non-leaded fuel, except where noted. The exhaust effluents from both the vehicle and engine were fed to similar polyvinyl chloride (PVC) dilution tubes which have been described in Section III-B. Separate dilution tubes were used for the vehicle and engine studies. Unless otherwise specified, stainless steel sampling probes were located in the dilution tube at the end remote from the air and exhaust inlets. All tests were made with the vehicle or engine operating under 60 mph road load, steady-state conditions.

Appendix A is a report on work carried out at Dow's expense prior to the current contract extension. This work led to the identification of the parameters being studied in Task I.

Experiments for Task I were run to evaluate the effects of various operating parameters as outlined below:

1. Effect of Dilution Tube Velocity
2. Effect of Filter Temperature
3. Effect of Dilution Air Temperature
4. Effect of Sample Probe Temperature
5. Effect of Sample Probe Location
6. Effect of Face Velocity Through the Filter Media
7. Effect of Sample Collection Time
8. Effect of Test Mode

It must be noted that in determining the effect of any one variable, it was extremely difficult to hold all other variables constant. Therefore, a complete analysis of the effect of each variable by itself can only be made by inference. In many cases, the same runs were used to try to evaluate several parameters. For example, the effect of the sample probe location was done on the same runs that were used to determine the effect of filter temperature.

3. Conclusions for Non-Leaded Fuel Particulate Sampling

a. A change in the temperature differential between the filter and the sample probe caused differences in amounts of collected particulate.

b. Changes in rate through the dilution tube caused slight variations in the amounts of particulate collected.

c. Dilution air temperature proved to be important since a lower temperature showed definite increases in the amount of particulate collected.

d. Sample probe location appeared to have only very small effects on particulate samples.

e. Face velocity of a sample stream through a given filter was important in that more sample, comparatively, tended to be collected at lower face velocities.

f. A majority of the sample, during a steady-state run, was collected within the first 25 percent of the time period over which the run was made.

g. Absolute measurements of grams/mile are misleading when measured during a steady-state run of long duration for the reason given in f above. Comparisons can be made, however, between runs of like time periods, and are valid as measurements of a trend.

h. The modified Federal cycle cold start gave more particulate than the 23 minute Federal cycle.

i. Most future work will be done at the following conditions:
   Filter temperature controlled to 100°F.
   Dilution tube velocity controlled to 400 ft/min.
   Inside dilution air used at all times.
   Sample will be collected on 142 mm filters.
   Steady-state runs will be 2 hours in duration.
   Filter rate will be 1 cfm.
   Sample probes will be used only at the end of the dilution tube.

4. Effects of Various Operating Parameters

Dilution Tube Velocity - The effect of velocity of the diluted exhaust in the dilution tube was studied in relation to the effect it might have on the amount of particulate collected. The raw data for this study is presented in Tables 10, 11, 12, and 13.

The dilution tube flow rate was varied from 300, 400, and 500 ft/min by using increased amounts of dilution air. Table 10 is a study of the true velocity effect in the tube at the three rates just mentioned. The flow rate would be expected to show some side wall effect and, in fact, does. Gas flow through the dilution tube was measured with an Anemotherm air meter manufactured by Anemostat Corporation of America. The general increase in measured flow as the velocity measuring device was inserted can be attributed to the turbulence created by the sampling probe itself, as well as some leakage at the lower end. The three sampling zones are described in Figure 7. The first sample zone was 9 feet from the point of entry of the exhaust; sample zone 2 was 16 feet; and, sample zone 3 was 23 feet.

Table 10
DILUTION TUBE FLOW RATE PROFILE

400 feet/min

Inches from Bottom of Tube	Sample Location		
	1	2	3
2	360 ft/min	390 ft/min	400 ft/min
4	360 ft/min	410 ft/min	410 ft/min
6	380 ft/min	410 ft/min	400 ft/min
8	380 ft/min	400 ft/min	400 ft/min
10	400 ft/min	400 ft/min	400 ft/min
12	400 ft/min	400 ft/min	410 ft/min
14	420 ft/min	400 ft/min	410 ft/min
15	420 ft/min	410 ft/min	430 ft/min

500 feet/min

	Sample Location		
	1	2	3
2	450 ft/min	490 ft/min	460 ft/min
4	470 ft/min	500 ft/min	500 ft/min
6	490 ft/min	500 ft/min	510 ft/min
8	500 ft/min	500 ft/min	510 ft/min
10	500 ft/min	500 ft/min	500 ft/min
12	500 ft/min	510 ft/min	500 ft/min
14	520 ft/min	510 ft/min	510 ft/min
15	500 ft/min	530 ft/min	510 ft/min

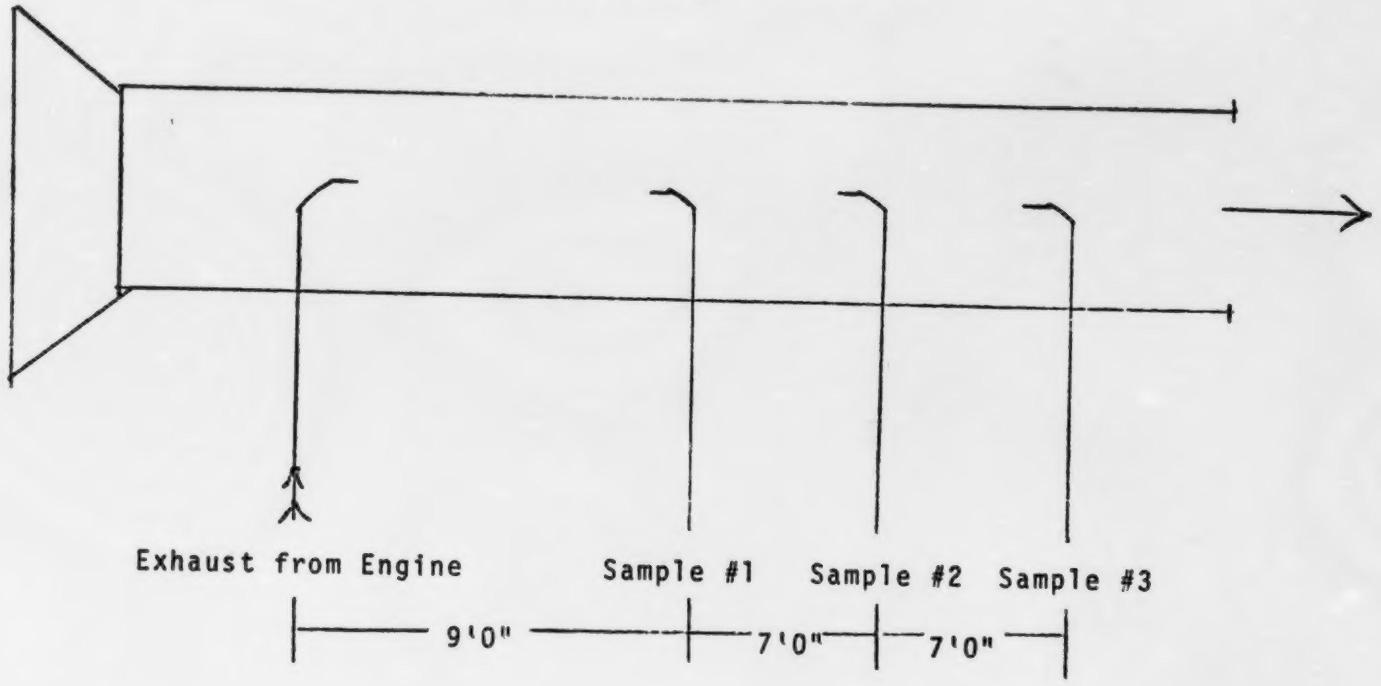
300 feet/min

	Sample Location		
	1	2	3
2	270 ft/min	280 ft/min	300 ft/min
4	280 ft/min	300 ft/min	300 ft/min
6	290 ft/min	300 ft/min	295 ft/min
8	280 ft/min	300 ft/min	290 ft/min
10	300 ft/min	300 ft/min	300 ft/min
12	300 ft/min	300 ft/min	305 ft/min
14	300 ft/min	320 ft/min	310 ft/min
15	330 ft/min	320 ft/min	350 ft/min

FIGURE 7

DILUTION TUBE SAMPLE POINTS

16" diameter Dilution Tube


Exhaust from Engine
Sample #1
Sample #2
Sample #3
9'0"
7'0"
7'0"

All the sampling of particulate to be analyzed was taken from the center of the tube (between 6 and 8 inches from the walls). The flow rates in this zone were quite constant at all three sampling points, indicating that complete mixing of the air and exhaust was taking place as close as 9 feet from the entry of the exhaust. Since the amount of exhaust remained constant while the amount of dilution air was varied, the temperature at various dilution rates also varied. Table 11 shows the effect of increased flow rate as well as the effect of temperature differences on the amounts of particulate collected. In all cases, except in the study of sample probe location, all samples were collected 23 feet from the exhaust inlet.

The following data, extracted from Table 11, shows that the rate of flow through the tube has a small effect on the grams/mile of particulate mass, independent of the temperature.

Flow Rate	Temperature (°F)	Grams	Grams/Mile
300	126	.0044	.0043
300	106	.0046	.0045
400	117	.0045	.0060
400	99	.0045	.0060
500	108	.0031	.0054
500	96	.0033	.0057

The grams/mile of particulate collected varied from a high of .0060 to a low of .0043, with the high point being 400 ft/min; 500 ft/min shows only a small decrease, which is within experimental deviation.

Table 12 shows the particulate collected using .5 cc/gal lead fuel at the same three flow rates. The low lead fuel was used to generate much higher amounts of particulate in

TABLE 11

DILUTION TUBE FLOW RATE COMPARISON, UNLEADED FUEL

	CFM Flow in the Dilution Tube	Exhaust Dilution Ratio	Dilution Tube Temp., °F at Sample Point - Avg.	Relative Humidity of Dilution Air:Room Temperature, °F	Temperature of the Dilution Air - Avg.	Relative Humidity at Filter (Calculated)	Dew Point at Dilution Tube Sample Point, °F (Calculated)	CFM Flow in 142 mm Filter	Temperature at Filter Surface, °F	Grams Particulate on Filter	Relative Humidity at the Sample Point in Dilution Tube - %	Grams per Mile Particulate	Filter Number
Air-Fuel Ratio (15.5)						400 Feet Per Minute							
Chassis Dynamometer	467	4.49:1	131.5	27/70	84	72	76	1.0	87.3	NG	20.0	-	1
1971 Chevrolet 350 CID	467	4.49:1	131.5	27/70	84	32	76	1.0	117.5	.0045	20.0	.0060	2
No TEL Fuel	467	4.49:1	131.5	27/70	84	49	76	1.0	99.9	.0045	20.0	.0060	3
60 MPH - SS - Run 90	467	4.49:1	131.5	27/70	84	58	76	1.0	94.3	.0040	20.0	.0054	4
												.0058	Avg.
Air-Fuel Ratio (15.3)						300 Feet Per Minute							
Chassis Dynamometer	342	3.24:1	141.0	30/69	75	99	85	1.0	86.0	NG*	20.0	-	1
1971 Chevrolet 350 CID	342	3.24:1	141.0	30/69	75	30	85	1.0	126.6	.0044	20.0	.0043	2
No TEL Fuel	342	3.24:1	141.0	30/69	75	52	85	1.0	106.0	.0046	20.0	.0045	3
60 MPH - SS - Run 91	342	3.24:1	141.0	30/69	75	80	85	1.0	95.2	NG	20.0	-	4
												.0044	Avg.
Air-Fuel Ratio (15.4)						500 Feet Per Minute							
Chassis Dynamometer	601	6.59:1	118.0	25.5/73	83.4	60	70	1.0	83.9	NG	22.5	-	1
1971 Chevrolet 350 CID	601	6.59:1	118.0	25.5/73	83.4	30	70	1.0	108.6	.0031	22.5	.0054	2
No TEL Fuel	601	6.59:1	118.0	25.5/73	89.4	44	70	1.0	96.2	.0033	22.5	.0057	3
60 MPH - SS - Run 92	601	6.59:1	118.0	25.5/73	83.4	52	70	1.0	88.5	.0036	22.5	.0062	4
												.0057	Avg.

*NG = no good, moisture on filter paper

Key: Filter #1 = Sample line water-cooled
#2 = Sample line insulated
#3 = Sample line water jacketed only
#4 = Sample line air-cooled

TABLE 12

DILUTION TUBE FLOW RATE COMPARISON
Low Lead Fuel

Flow ft/min	Flow in Tube cfm	Exhaust Dilution Ratio	Temperature at Filter Surface	Grams Particulate on Filter	Grams/Mile
400	445	4.49:1	114°F	.0087	.0322
300	330	3.24:1	116°F	.0095	.0261
500	580	6.59:1	104°F	.0072	.0348

Runs 100A, 100B, 100C

All runs on chassis dynamometer, 1971 Chevrolet 350 CID
0.5 cc TEL fuel, 60 mph Steady-state, 6 hour sampling time,
142 mm, 1 cfm filter

order to help minimize any deviations due to experimental error. The temperature effects were minimized also. The grams/mile of particulate mass increased from 0.0261 g to 0.0348 g as the flow went from 300 to 500 ft/min. This data is shown graphically in Figure 8.

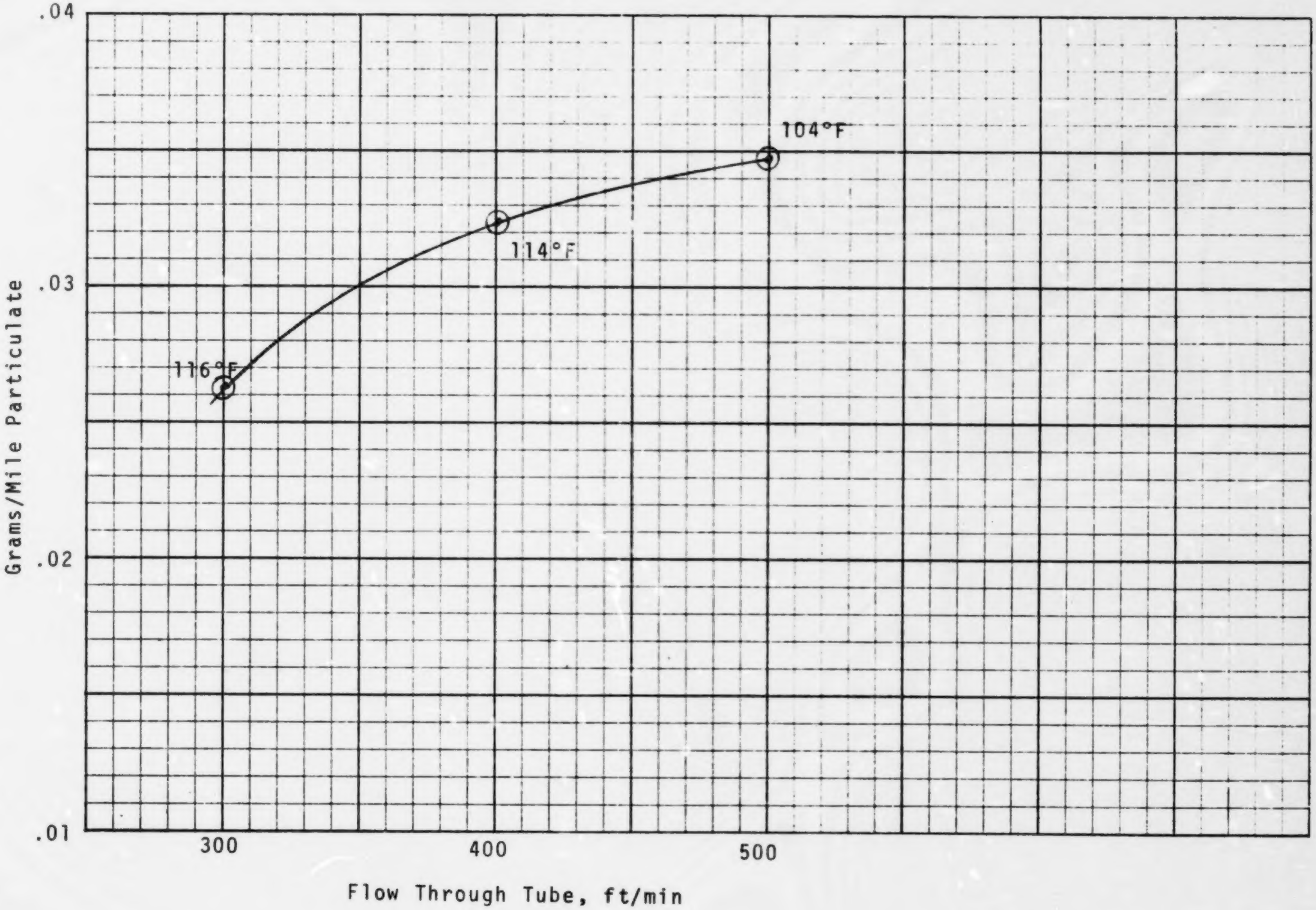
Comparing Runs 90, 91, and 92 (Table 11) to Runs 100A, 100B, and 100C (Table 12) shows an increase of 24 percent in grams/mile of particulate mass in the first case, and an increase of 25 percent in the second, going from 300 ft/min to 500 ft/min. All of the runs in Table 12 were done on the same day, thus minimizing any ambient temperature or humidity differences.

Table 13 shows again the effect of flow rate versus particulate collected. In this experiment, temperature differences between flow rates, at the same sample points, were small. In each case, the grams/mile of particulate mass appeared somewhat higher at 500 ft/min, but some of the effect was probably due to the small difference in temperature.

Conclusions

The differences in the amount of particulate collected at the three flow rates studies were small enough so that a flow rate of 400 ft/min was settled on as the rate for future work. The differences between the flow rates were attributed more to the temperature differences than to any fundamental change due to the exhaust dilution.

Effect of Filter Temperature - Earlier attempts at defining some of the variables in the dilution tube method of collecting particulate samples indicated that the temperature of the gas stream being sampled, at the filter, had an effect on the amount of particulate collected. The data shown in Tables 14 and 15 were generated as an attempt to further characterize the filter temperature effect.



Dilution Tube Velocity vs. Grams/Mile Particulate

Figure 8

TABLE 13

DILUTION TUBE FLOW RATE COMPARISON, NON-LEADED FUEL

Ft/Min Flow in Tube	Sampling Point Temperature	SAMPLE LINE					
		Heated		Ambient		Cooled	
		Temp. @ Filter	g/Mile Collected	Temp. @ Filter	g/Mile Collected	Temp. @ Filter	g/Mile Collected
300	132.8°F	125°F	.0049	108°F	.0060	82°F	.0064
500	109.4°F	111°F	.0056	97°F	.0070	81°F	.0070

Runs 113B and 113C
All runs made on 1972 Pontiac 400 CID engine dynamometer.

No lead fuel, 60 mph steady-state, 2 hour sample time.

142 mm, 1 cfm filter.

TABLE 14
FILTER TEMPERATURE EFFECT ON PARTICULATE

Temperature at Filter (°F)	Flow Rate in Tube Feet/Minute	Grams/Particulate on Filter	Grams/Mile
106	300	.0046	.0043
126	300	.0044	.0045
94	400	.0040	.0054
99	400	.0045	.0060
117	400	.0045	.0060
88	500	.0036	.0062
96	500	.0033	.0057
109	500	.0031	.0054

Run on 1971 Chevrolet, 350 CID

Non-leaded fuel, 5.75 hours, 60 mph

Steady-state

TABLE 15

FILTER TEMPERATURE EFFECT ON PARTICULATE

		Sample Zone 1		Sample Zone 2		Sample Zone 3	
Run No.	Flow Rate	Temp. Before Filter	Grams Collected	Temp. Before Filter	Grams Collected	Temp. Before Filter	Grams Collected
107	300	122°F	.0087	111°F	.0085	113°F	.0092
105	400	106°F	.0094	102°F	.0095	100°F	.0098
102	400	86°F	.0075	100°F	.0073	104°F	.0086
106	500	100°F	.0065	100°F	.0065	100°F	.0061

Runs 102, 105, 106, 107
All runs made on 1972 Pontiac 400 CID engine dynamometer
Non-leaded fuel, 60 mph steady-state, sample time 4 hours
142 mm, 1 cfm filter

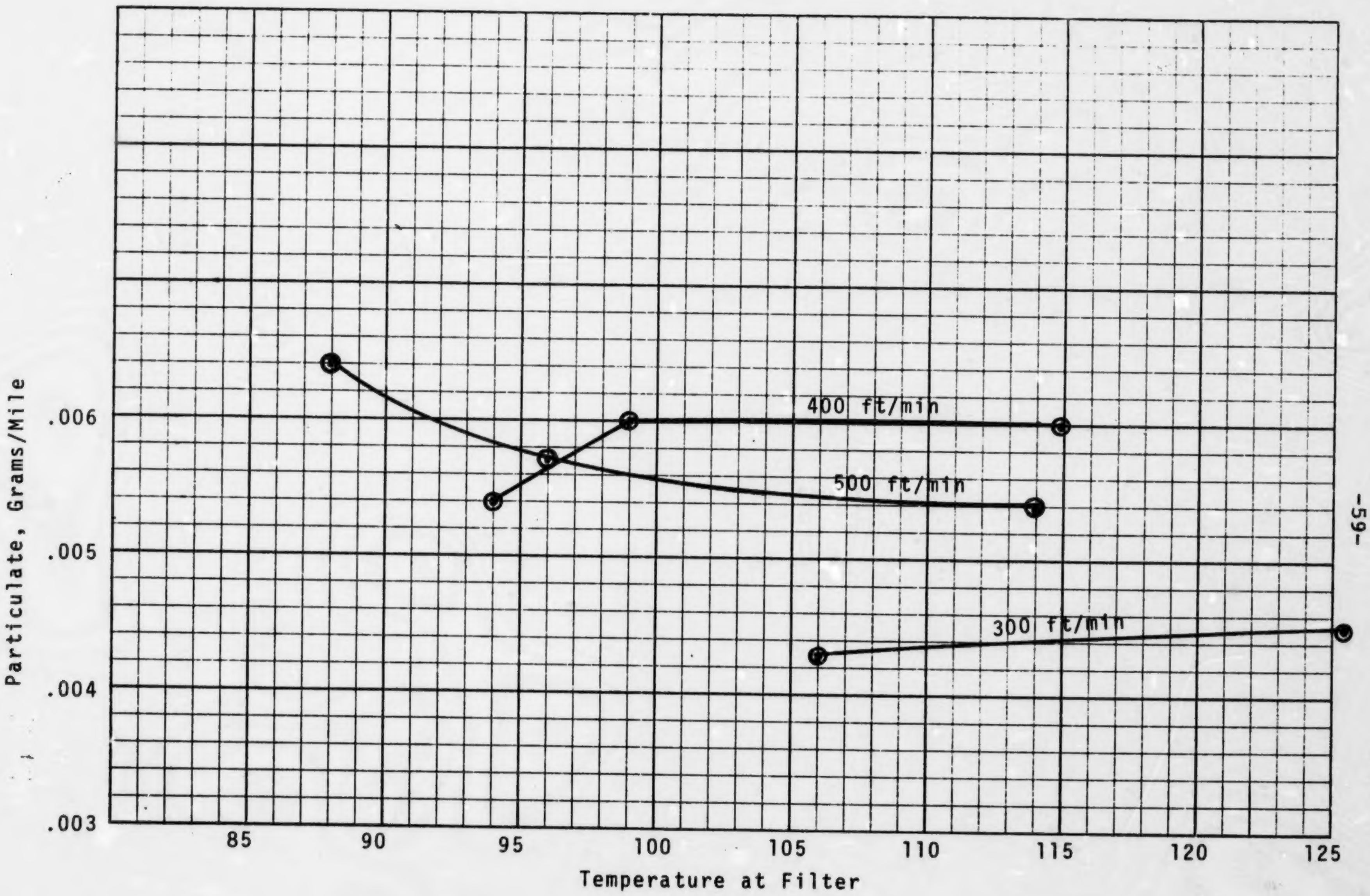
At 400 ft/min flow, a change in temperature from 117°F in an insulated sample line to 99°F in a water-jacketed line showed no change in grams/mile of particulate mass collected. A change from 126°F to 106°F showed a change of only 0.0002 grams out of 0.0045 grams collected. Changes from 109°F to 96°F to 88.5°F showed weights of 0.0054 g, 0.0057 g, and 0.0062 g. These changes are quite small, although it is felt that they are meaningful. In all cases, the higher temperatures tended to give the least amount of sample collected. However, grams/mile of particulate mass tended to stay close to being constant with temperature change. This effect is shown in Figure 9.

Table 15 shows a reversal of the above observation, however. Note that in sample Zone 1 (not normally used in particulate samplings), at 400 ft/min an increase in temperature from 86°F to 106°F gave an increase of 0.0019 g particulate. It is felt that the results of Run 105 (ambient conditions, etc.) were, for some reason, not comparable to Run 102. In both cases, the runs were consistent with themselves with respect to sample probe location. The data is plotted as a function of temperature versus particulate mass in Figure 10. There does not appear to be a clear trend in particulate collected based on temperature effects.

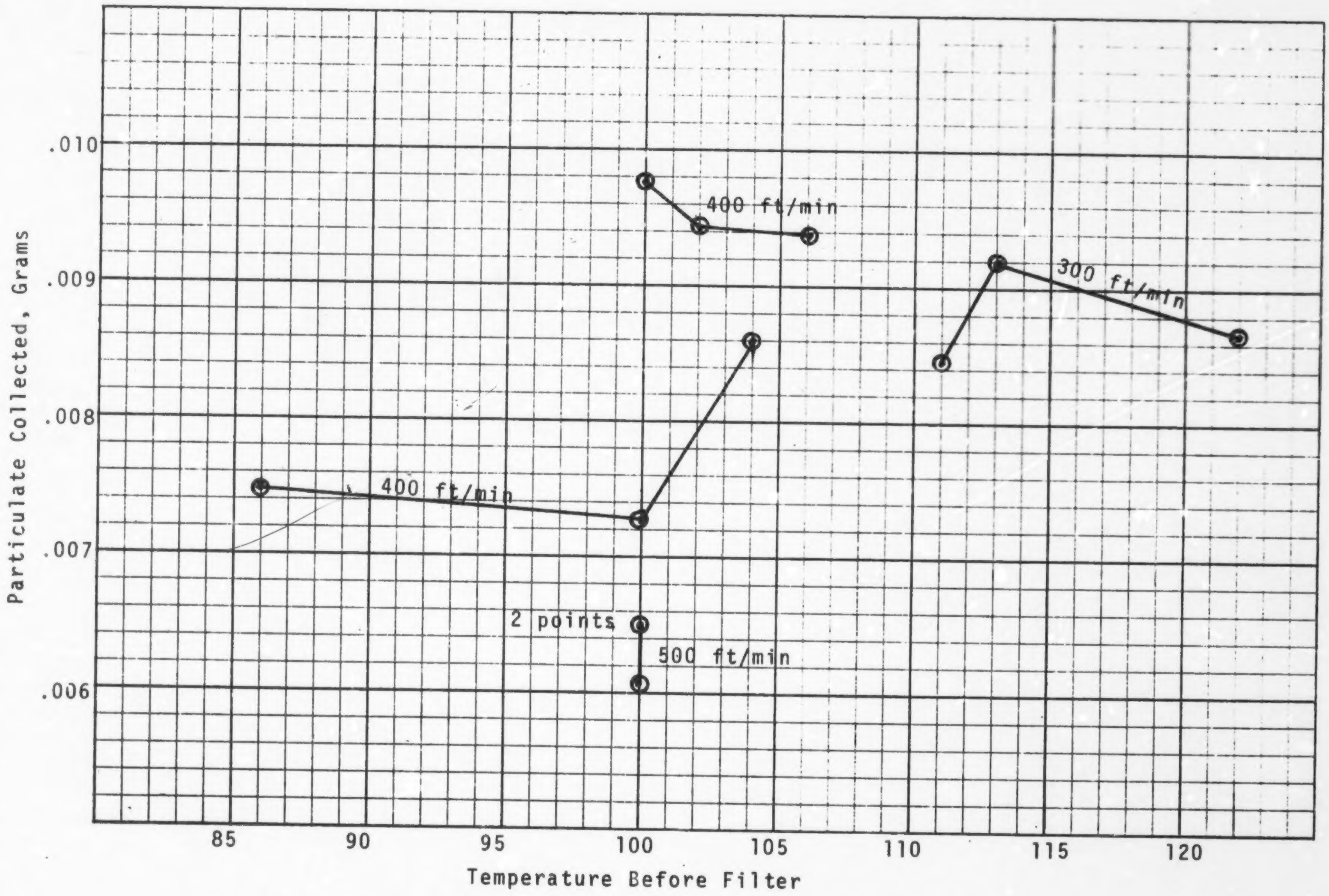
Past experience on particulate sampling has shown that approaching the dew point of the diluted exhaust stream has a definite effect on the particulate picked up by the filters. These runs were all sampled above the dew point.

Conclusions

Available data indicate that the higher filter temperatures are likely to lead to lower amounts of particulate collected. For that reason, the filter probe temperature was maintained at 100°F



EFFECT OF FILTER TEMPERATURE CHANGE ON GRAMS/MILE
Figure 9



EFFECT OF FILTER TEMPERATURE ON COLLECTED PARTICULATE MASS

Figure 10

by water jacketing the probes. This temperature was at least 20°F above the dew point of a run at 400 ft/min. The temperature of the diluted exhaust at 400 ft/min, using indoor diluent air, is generally above 100°F with no external controls. Cooling was almost always necessary to give an average of 100°F. Under conditions of the Federal cycle cold start, the sample probes were warmed to keep them at 100°F during the first part of the run.

Effect of Dilution Air Temperature - Table 16 contains a tabulation of data generated to assess the effect of using cooler outside air as a dilution for the exhaust rather than warmer inside air. During the course of these runs, the ambient air being used for dilution was about 40°F, or roughly 35-40°F cooler than internal air.

Under comparable conditions of flow rate, the grams/mile of particulate mass collected showed a 23 percent and a 17 percent increase using cool air compared to warm air. This effect was expected since previous experience had shown that some percentage of the particulate component was due to condensed material, which increased in amount as temperatures were lowered.

Since the ambient air was uncontrollable and since the temperature of the total diluted exhaust stream was difficult to change except by changing the temperature of the diluent, all additional work was done using room air for a diluent. However, since the temperature effect is real, any condition of cold starting can be expected to give larger amounts of particulate than would the corresponding hot start, since the total diluted exhaust stream is lower in temperature until the engine reaches operating temperature.

TABLE 16

EFFECT OF DILUTION AIR TEMPERATURE ON GRAMS/MILE

Run	Ft/Min Flow in Tube	Corrected Flow, cfm	Dilution Tube Temperature	Grams Collected	g/Mile Collected	Dilution Air
109A	400	479	120°F	.0066	.0351	Inside
109B	400	509	92°F	.0077	.0432	Outside
110A	400	506	95°F	.0085	.0478	Outside
110B	400	477	122°F	.0077	.0408	Inside

All runs made on 1972 Pontiac 400 CID engine dynamometer
Non-leaded fuel, 60 mph steady-state, 3 hour runs
Average of three filters

Conclusions

A lower diluted exhaust stream temperature results in higher amounts of collected particulate. Attempts to control this variable will be made by using only inside air for a diluent.

Effect of Sample Probe Temperature - Table 17 contains the results of several tests to determine the effect of varying the temperature of the sample probe. Water jackets were installed on the tubes used as sample probes allowing either cooling or heating to determine any differences. Runs were made at 300, 400, and 500 ft/min. The 400 ft/min run was not good since the sample collection temperature dropped below the dew point, giving meaningless results.

In comparing the effect of a drop in sample probe temperature at constant flow through the dilution chamber, it was shown that a cooler sample probe, resulting in cooler temperatures at the filter, does cause an increase in collected particulate. This experiment is very closely related to the determination of the effect of filter temperature previously discussed, and further verifies the conclusions drawn from those runs. The data is plotted in Figure 11.

Although the increase in collected particulate continues to temperatures below 100°F, this temperature was felt to be the lower limit of confidence with respect to maintaining an adequate spread between dew point and filter temperature. Most future work was done with the sample lines jacketed and controlled to about 100°F filter temperature.

Effect of Sample Probe Location - The Dow dilution tube is 23 feet long from where the exhaust enters the tube to where the majority of the sampling has been done. It was felt that there might be an effect on the amount of particulate collected due to sample probe location.

TABLE 17

EFFECT OF SAMPLE PROBE TEMPERATURE

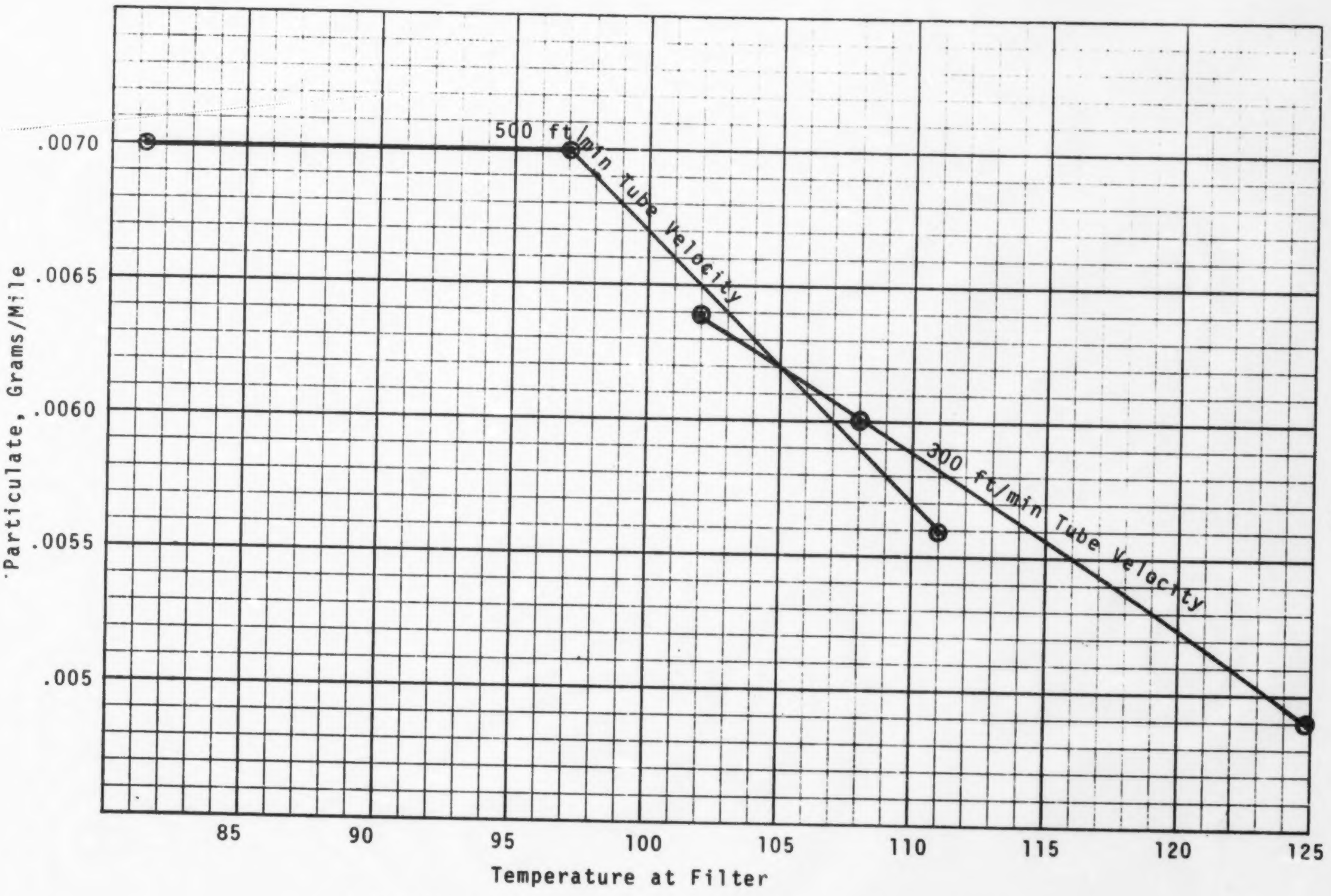
		SAMPLE ZONE					
		Heated		Ambient		Cooled	
Ft/Min Flow in Tube	Sampling Point Temperature	Temp. @ Filter	g/Mile Collected	Temp. @ Filter	g/Mile Collected	Temp. @ Filter	g/Mile Collected
300	132.8°F	125°F	.0049	108°F	.0060	82°F	.0064
500	109.4°F	111°F	.0056	97°F	.0070	81°F	.0070

Runs 113B and 113C

All runs made on 1972 Pontiac 400 CID engine dynamometer

Non-leaded fuel, 60 mph steady-state, 2 hour sample time

142 mm, 1 cfm filter



SAMPLE PROBE TEMPERATURE vs. GRAMS/MILE PARTICULATE
Figure 11

Figure 7 is a schematic diagram of the dilution tube and the three sample zones tested. In Table 18, the data for each of the zones at a specific flow rate is tabulated. In general, the effect of sample probe location is shown to be slight; for example, Run 105 at 400 ft/min shows a range of .0094 g to .0098 g of particulate collected across the three sample zones. There was a slight temperature decrease across the three zones which was felt to be more likely the cause of the slight sample size increase than was any effect due to location. Run 106 shows again a very slight decrease in collected sample at essentially constant temperature. The data is graphed in Figure 12.

Conclusions

There appeared to be no large effect in particulate sample size due to sample probe location. In all further work, samples will be taken only at Zone 3, which is 23 feet from the point of entry of the exhaust.

Effect of Face Velocity Through the Filter Media - Table 19 is a tabulation of the data collected using a 142 mm glass fiber filter at varying flow rates. As is clearly shown, the gross amount of raw sample collected increases as the flow increases. However, when the data was calculated on a grams/mile basis, the slower rate of collection gives much higher numbers. Figures 13 and 14 show this graphically.

Although no attempt was made to keep the sample probe or filter temperature constant, and although we have noted a temperature effect on sample size in previous work, it was felt that the effect noticed in this instance was much greater than would be expected from the temperature differences noted.

TABLE 18

EFFECT OF SAMPLE PROBE LOCATION

Run No.	Flow Rate	Sample Zone 1		Sample Zone 2		Sample Zone 3	
		Temp. Before Filter	Grams Collected	Temp. Before Filter	Grams Collected	Temp. Before Filter	Grams Collected
107	300	122°F	.0087	111°F	.0085	113°F	.0092
105	400	106°F	.0094	102°F	.0095	100°F	.0098
102	400	86°F	.0075	100°F	.0073	104°F	.0086
106	500	100°F	.0065	100°F	.0065	100°F	.0061

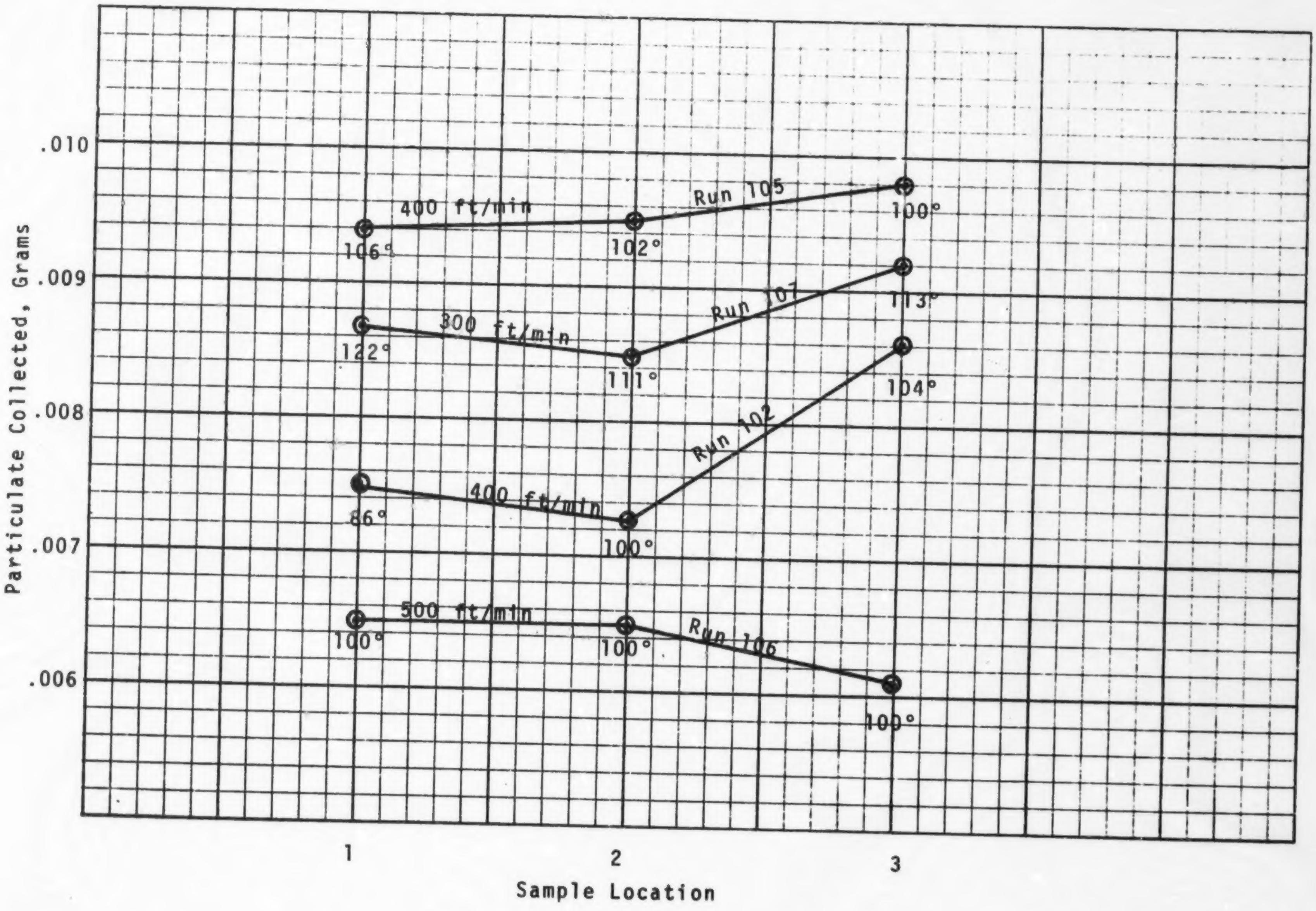
All runs made on 1972 Pontiac 400 CID engine dynamometer
Non-leaded fuel, 60 mph steady-state, sample time 4 hours
142 mm, 1 cfm filter

TABLE 19

EFFECT OF FLOW RATES THROUGH FILTER MEDIA

Run	Grams Collected	Flow at Filter	Temperature at Filter	Grams Equilibrated to 1 cfm	Grams/Mile
96	.0045	0.5 cfm	81°F	.0090	.0394
96	.0053	1 cfm	104°F	.0053	.0232
96	.0057	2 cfm	115°F	.0028	.0125
96	.0066	4 cfm	125°F	.0016	.0072
98	.0051	0.5 cfm	91°F	.0102	.0446
98	.0051	1 cfm	100°F	.0051	.0223
98	.0054	2 cfm	117°F	.0027	.0118
98	.0072	4 cfm	126°F	.0018	.0079

All runs on 1971 Chevrolet 350 CID chassis dynamometer
Non-leaded fuel, 60 mph steady-state, 2 hours
142 mm glass filter



EFFECT OF SAMPLE PROBE LOCATION
Figure 12

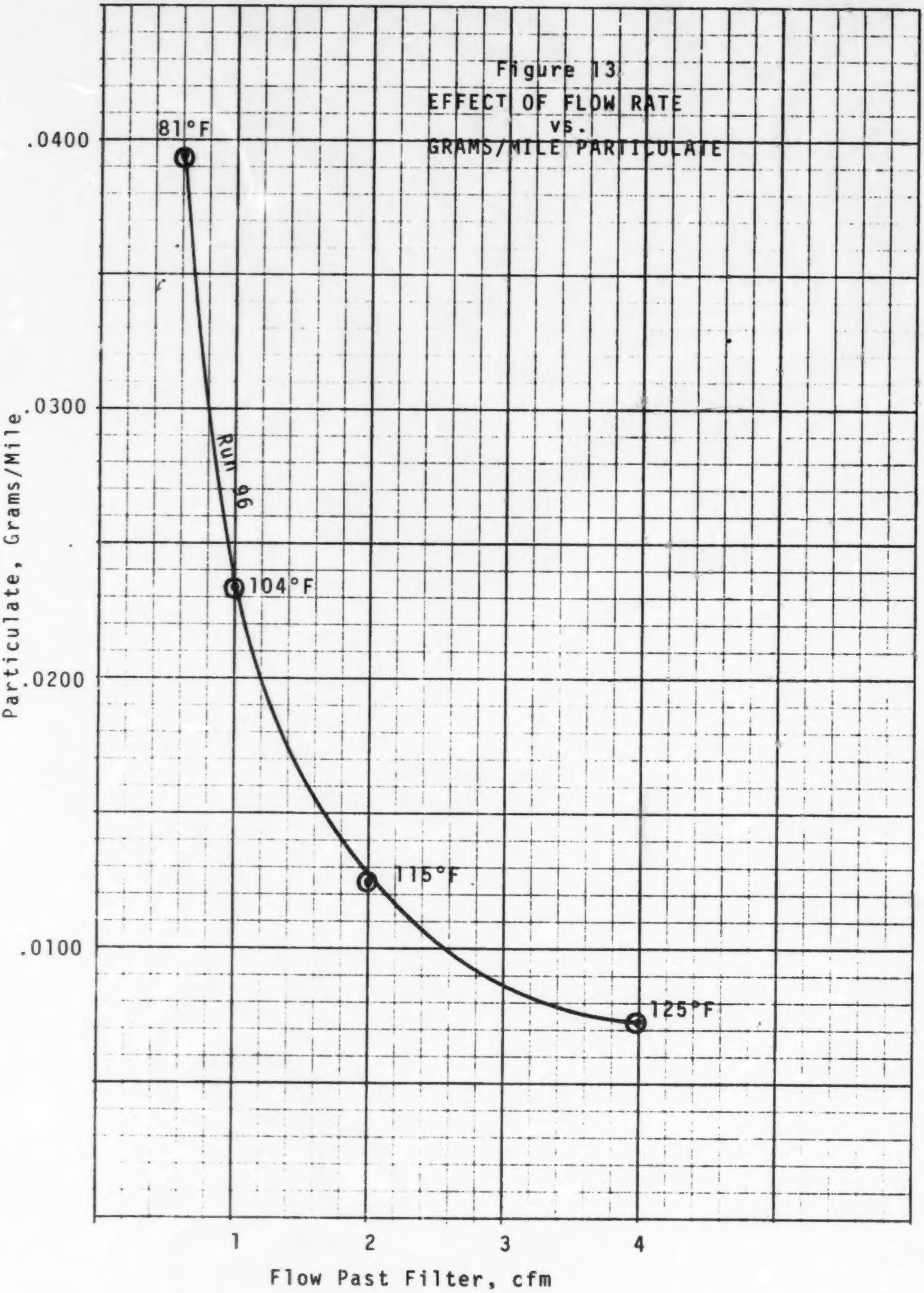


Figure 13
EFFECT OF FLOW RATE
vs.
GRAMS/MILE PARTICULATE
Particulate, Grams/Mile
.0400
.0300
.0200
.0100
Flow Past Filter, cfm
1
2
3
4
81°F
104°F
115°F
125°F
Run 96

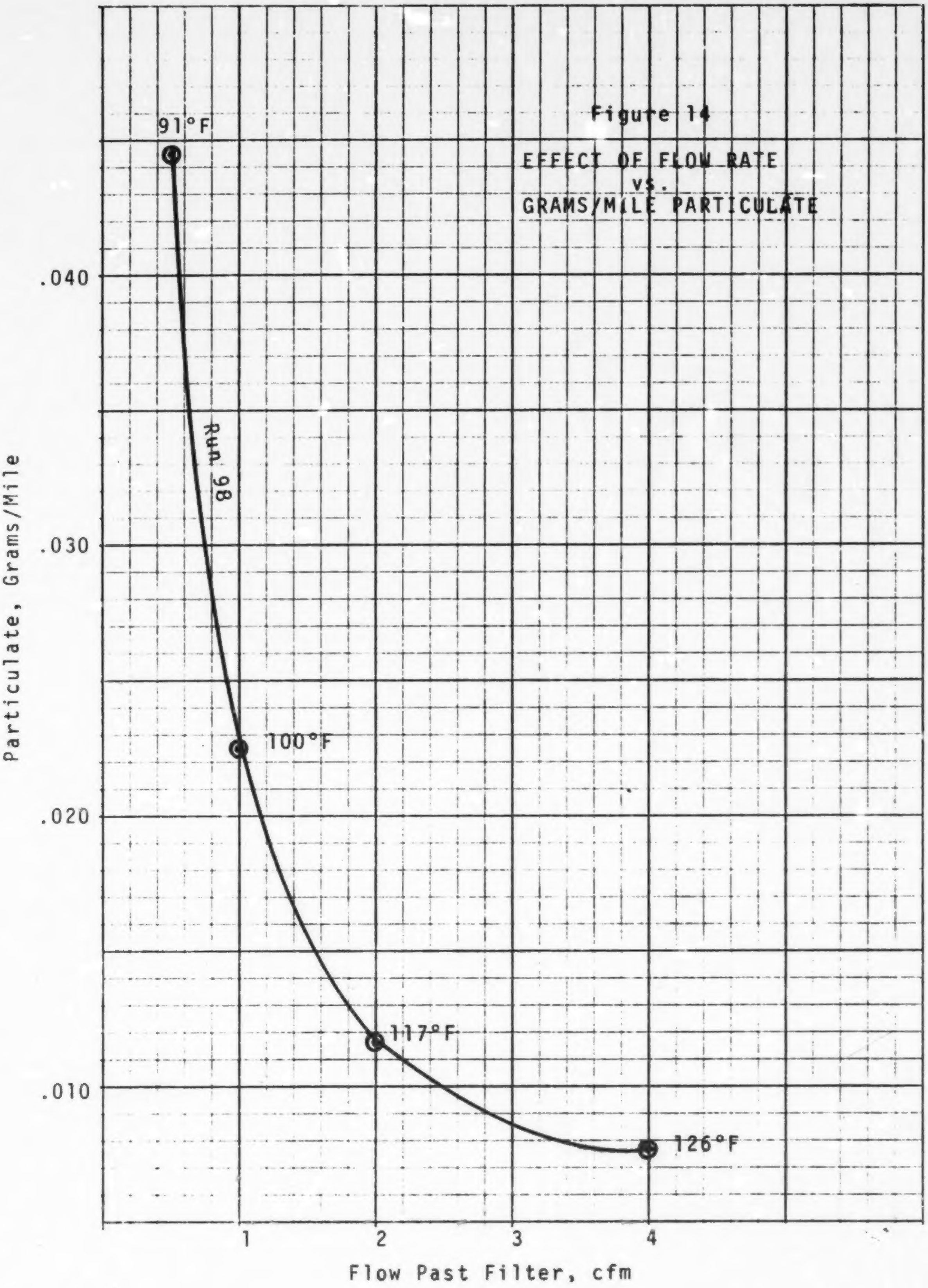


Figure 14

EFFECT OF FLOW RATE
vs.
GRAMS/MILE PARTICULATE

Table 20 is a measure of the effect of face velocity through the filter obtained by varying filter diameter.

The collection of particulate sample at 1 cfm through the 142 mm filter was felt to be the best operating rate since the additional amount of sample collected at the higher rates was offset by the difficulty of maintaining these flow rates at a temperature near 100°F. In addition, when calculated on a grams/mile basis, the higher flow rates show a much lower number.

Conclusions

High face velocity through the filter media leads to comparatively less sample collected. A rate of 1 cfm through the 142 mm filter will be used in future work.

Effect of Sample Collection Time - Table 21 is a tabulation of several runs made to determine the effect of sample collection time on the amount of particulate collected. As would be expected, the longer collection times did result in more sample collected. However, the rate of sample collection was much higher in the initial few minutes of the collection period than in the final few minutes. The data from Runs 99, 101, 104, and 108 (calculated in grams/mile) are presented graphically in Figures 15, 16, 17, and 18.

The raw data from Run 108 shows about 22 percent of a 2-hour sampling period being collected in the first 5 minutes. It was obvious, therefore, that any attempt to attach quantitative significance to the particulate mass grams/mile figure must be done with extreme caution. If all sampling parameters are held constant except one, comparative significance can be inferred from a grams/mile calculation.

TABLE 20

EFFECT OF FACE VELOCITY THROUGH FILTER

Filter Diameter	Flow Through Filter	Grams Particulate	Face Velocity
142 mm	1 cfm	.0022	7.346 ft/min
47 mm	1 cfm	.0007	96.8 ft/min
293 mm	1 cfm	.0045	0.5208 ft/min

Run made on 1971 Chevrolet, 350 CID chassis dynamometer
Non-leaded fuel, 60 mph steady-state, 3 hours

TABLE 21
EFFECT OF SAMPLE COLLECTION TIME ON GRAMS/MILE

Run	Filter Time	Grams Collected	Grams/Mile
99	0.5 hr	.0039	.0682
99	1.0 hr	.0056	.0470
99	1.5 hr	.0070	.0408
99	2.0 hr	.0081	.0354
99	1.0 hr	.0055	.0481
99	0.5 hr	.0036	.0630
101	0.5 hr	.0048	.0840
101	1.0 hr	.0070	.0612
101	1.5 hr	.0072	.0420
101	2.0 hr	.0089	.0389
104	5 min	.0013	.1356
104	10 min	.0023	.1206
104	20 min	.0046	.1206
104	30 min	.0058	.1014
104	5 min	.0015	.1572
104	10 min	.0026	.1362
104	20 min	.0044	.1155
104	30 min	.0061	.1066
108	5 min	.0013	.1365
108	10 min	.0022	.1152
108	20 min	.0034	.0891
108	30 min	.0037	.0646
108	1.0 hr	.0047	.0411
108	1.5 hr	.0054	.0314
108	2.0 hr	.0060	.0263

All runs on 1971 Chevrolet 350 CID chassis dynamometer
0.5 cc lead fuel except Run 108 which was non-leaded fuel
60 mph steady-state
142 mm, 1 cfm filter

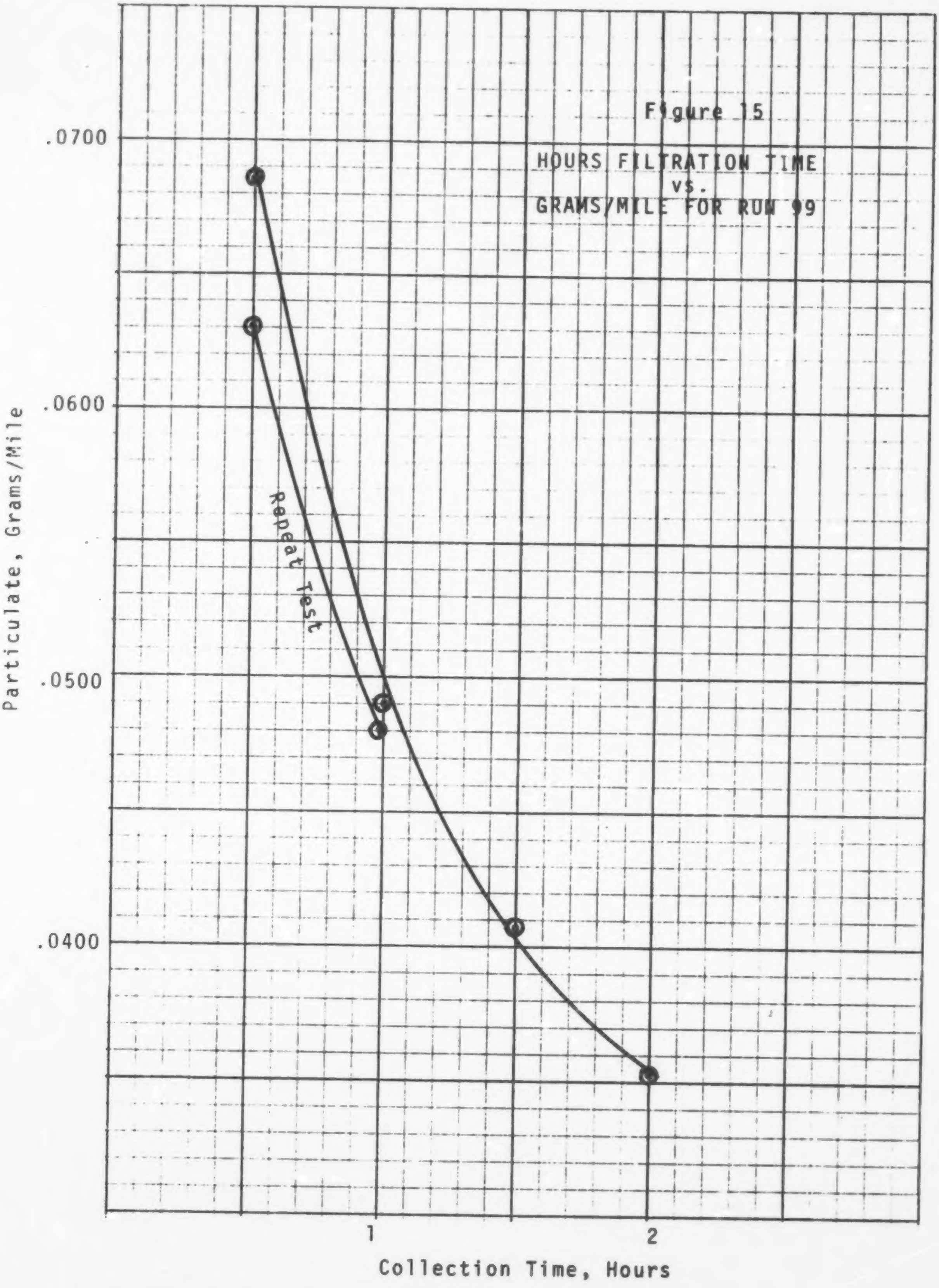


Figure 15
HOURS FILTRATION TIME
vs.
GRAMS/MILE FOR RUN 99
Repeat Test
.0700
.0600
.0500
.0400
Particulate, Grams/Mile
1
2
Collection Time, Hours

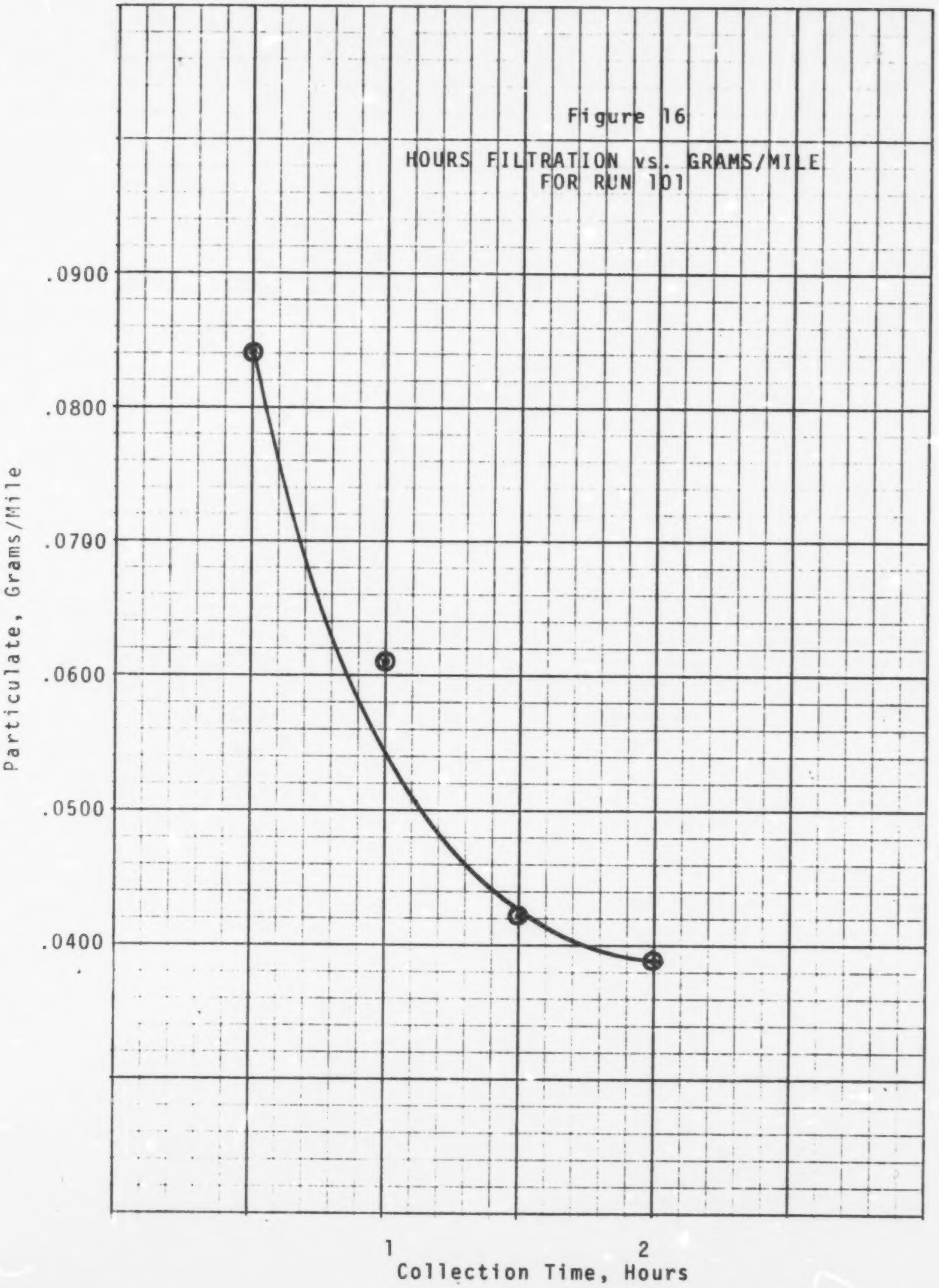


Figure 16

HOURS FILTRATION vs. GRAMS/MILE FOR RUN 101

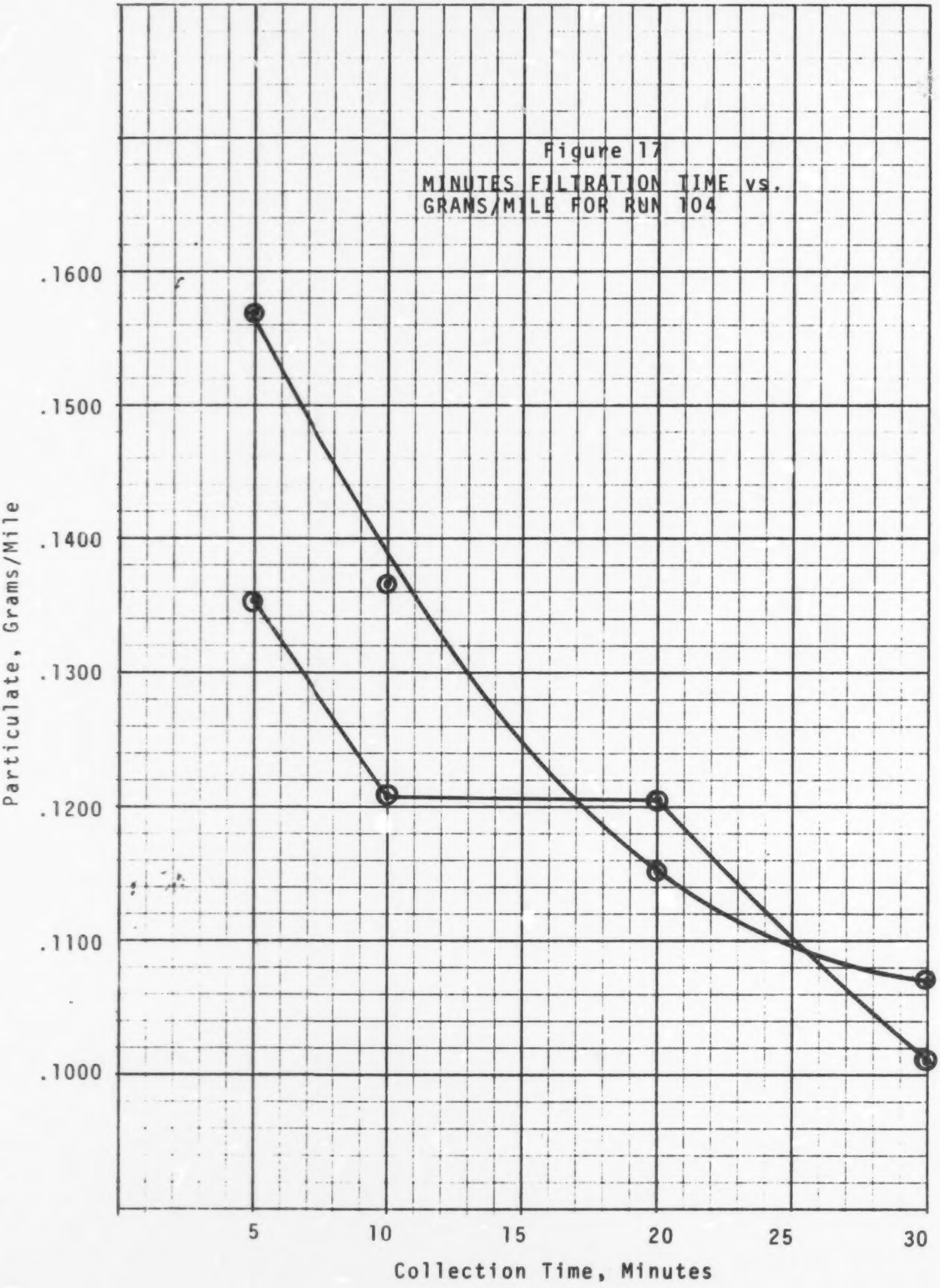


Figure 17

MINUTES FILTRATION TIME vs.
GRAMS/MILE FOR RUN 104

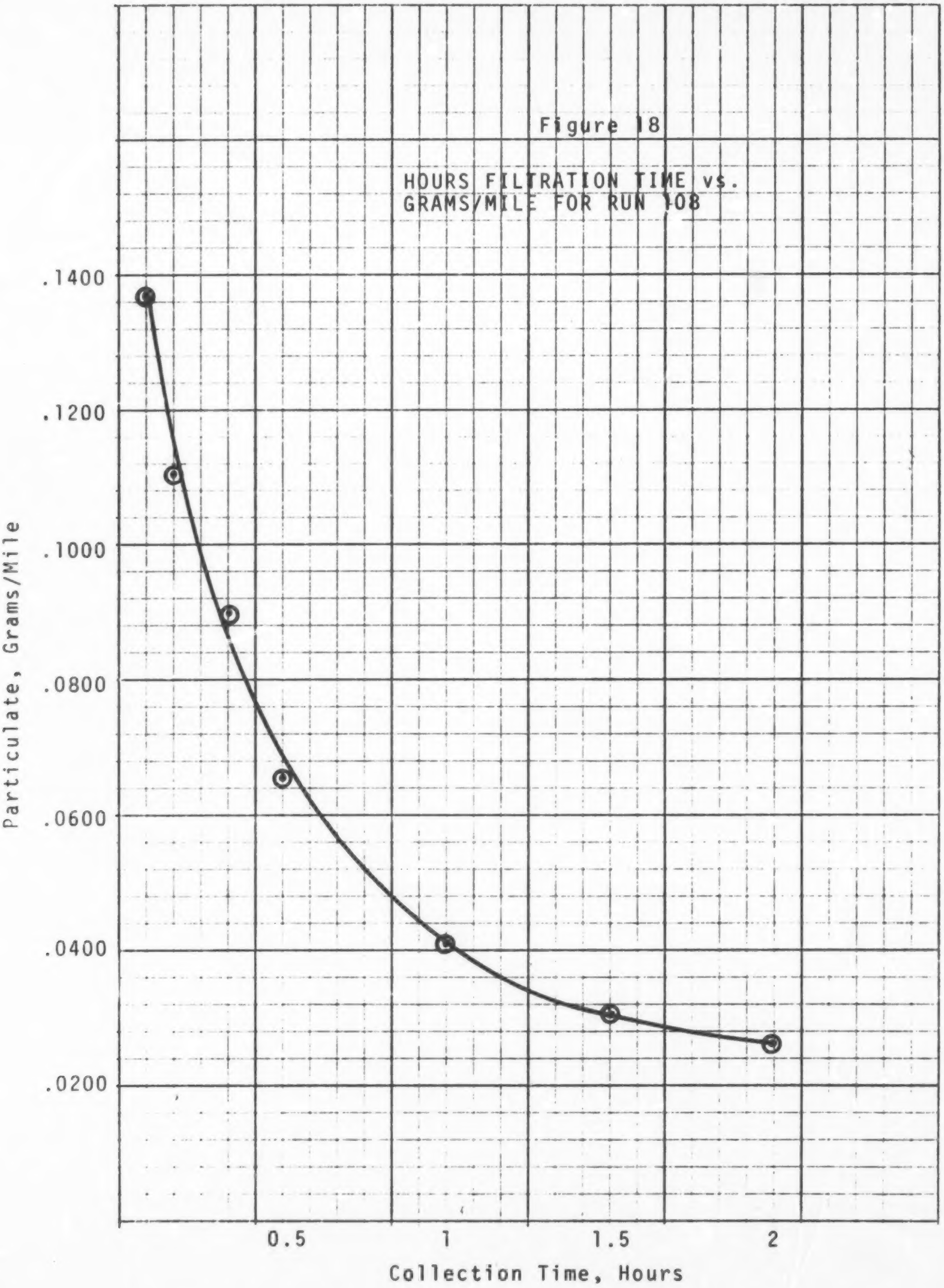


Figure 18

HOURS FILTRATION TIME vs.
GRAMS/MILE FOR RUN 108

In order to obtain sufficient raw sample for analysis, future work will generally be done using a 2-hour steady-state collection period, except where a Federal or other cycle is noted.

> Conclusions
>
> The sample collection period has a definite effect on sample size, with a large amount of the sample being collected in the first few minutes. Grams/mile figures of particulate mass are, therefore, misleading unless used only in a comparative sense.

Effect of Test Mode - A series of tests were made to determine the amount of particulate collected during the 23 minute Federal cycle versus the 41.4 minute modified Federal cycle. In previous runs it was noted that similar weights were obtained in both the 23 minute and the modified cycle.

Table 22 is a tabulation of the results and outline of the procedure used to verify any differences. The tests were run on the same day and with all variables essentially constant. After a 23 minute cold start, 0.0014 g of particulate mass were collected and after the additional run of 505 seconds, a total of 0.0020 g were collected. This verified that somewhat more sample was collected during the latter part of the modified run.

Tube air (filtered) was drawn through the dilution chamber and the filter during part of the test to determine the effect, if any, of the additional time of flow past the filter surface. It appears that this effect was negligible.

TABLE 22

EFFECT OF TEST MODE ON PARTICULATE COLLECTED

Procedure for Run 111
Federal Cycle Cold Start Modified

Filter #1	Filter #2	Filter #3	Filter #4
Cold start 23 min	Cold start 23 min	Cold start 23 min	Cold start 23 min
↓	↓	↓	↓
10 min tube air	Filter OFF during 10 min shutdown	10 min tube air	Stop - weigh paper .0014 grams
↓	↓	↓	↓
505 sec hot start	Filter ON again. 505 sec hot start	Stop - weigh paper	Replace used paper into filter. Using pre-filtered air, draw 1 cfm room air through filter for 10 min .0014 grams
↓	↓	↓	↓
Stop - weigh paper	Stop - weigh paper	END	Stop - re-weigh paper
↓	↓		↓
END	END		If paper is not damaged replace in filter. Continue room air for 30 min .0012 grams
			↓
.0020 grams	.0020 grams	.0014 grams	Stop - re-weigh paper
			↓
			END

Run made on 1971 Chevrolet 350 CID chassis dynamometer

Non-leaded fuel

142 mm filter, 1 cfm

B. TASK II

1. Introduction

The major objective in Task II was to establish the baseline data for the Pontiac 400 CID engine using low lead (0.5 cc/gal) and unleaded fuel.

The data for the non-leaded fuel runs are presented in Table 23 and for leaded fuel in Table 24.

2. Conclusions

a. In general, the low lead fuel gave higher particulate levels, in grams/mile of particulate mass, than the non-leaded fuel.

b. Overall, the aldehyde content of the exhaust condensate was not significantly different between the non-leaded and low lead fuel.

c. The concentration of benzo-α-pyrene in the particulate varied widely with engine conditions, but did not appear to be significantly changed by use of leaded versus unleaded fuel.

d. Air/fuel ratio had an effect on particulate with the standard setting generally being lower than either rich or lean settings.

e. The effect on particulate due to changes in spark timing is sporadic and, therefore, inconclusive based on this data.

f. In almost all cases, 30 mph at steady-state gave 50-100 percent higher particulate mass levels than the corresponding 60 mph run.

TABLE 23

ENGINE DYNAMOMETER TEST OF CONVERTER EQUIPPED ENGINES

Engine Type: 1972 Pontiac 400 CID
Fuel Used: Indolene #15214 - No lead 91 octane
Converter Type: None

Run No.	Air to Fuel Range	Air to Fuel Actual	Test Mode	Spark Timing	Grams/Mile Particulate 1 cfm Filter	Converter Temp. (°F)	Dilution Tube Temp. (°F)	Filter Temp. (°F)	ppm in Exhaust Condensate HCHO	ppm in Exhaust Condensate NH_3
155A	L	17.1	30 mph CS	Std	.0757	-	93.0	100-102	613	-
128A	L	15.0	30 mph HS	Std	.0338	-	93.2	100-102	300	5
128B	L	16.7	60 mph HS	Std	.0218	-	147	93-96	400	16
158C	S	14.7	30 mph HS	Adv	.0284	-	91.4	102-105	660	-
126A	S	14.7	30 mph HS	Std	.0238	-	95.0	100-105	210	6
158A	S	14.5	30 mph HS	Ret	.0260	-	91.0	100-107	410	-
156A	S	15.5	30 mph CS	Std	.0445	-	87.8	97-100	591	-
130C	S	15.1	60 mph HS	Adv	.0420	-	140	88-96	1530	13
130A	S	15.1	60 mph HS	Std	.0167	-	143	86-100	360	10
130B	S	15.1	60 mph HS	Ret	.0117	-	149	90-100	150	10
126B	S	-	Dow Cycle 2	Std	.0209	-	91.4	96-100	230	12
126B	S	-	Dow Cycle 3	Std	.0209	-				
126B	S	-	Dow Cycle 4	Std	.0209	-				
126B	S	-	Dow Cycle 5	Std	.0209	-				
129A	R	13.7	30 mph HS	Std	.0387	-	91.4	99-100	250	6
129B	R	12.7	60 mph HS	Std	.0255	-	136.4	102-104	150	14

Spark setting: Adv = Std -10°
Ret = Std +10°

Continuation of Table 23

ANALYSIS OF EXHAUST GAS

	% by Volume				Parts per Million			
Run No.	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x
155A	9.0	10.35	79.7	.03	115	200	425	-
128A	11.1	7.0	80.9	.03	189	850	270	-
128B	12.0	5.7	81.4	.03	78	850	330	-
158C	13.8	3.2	82.3	.03	210	56	2100	-
126A	11.7	4.5	82.8	.03	275	850	260	-
158A	13.7	3.4	82.2	.03	150	32	650	-
156A	12.2	5.2	81.5	.05	316	65	960	-
130C	11.3	6.5	81.1	.17	830	1300	650	-
130A	12.9	3.5	82.3	.43	145	850	575	-
130B	12.7	4.3	82.0	.03	43	900	340	-
126B	10.3	7.6	81.2	.03	265	-	-	-
126B	11.2	6.1	81.7	.03	145	-	-	-
126B	9.4	9.3	80.4	.03	218	-	-	-
126B	11.1	6.0	82.0	.03	300	-	-	-
129A	13.4	2.9	82.4	.31	268	400	1100	-
129B	11.9	3.5	81.7	1.95	305	360	1500	-

Continuation of Table 23

ANALYSIS OF EXHAUST PARTICULATE

Run	Trace Metals on Millipore Filter (% of particulate)											Measured in Particulate		
No.	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	% Pb Atomic Absorp	% C on Glass Filter	ppm BaP
155A	-	-	-	-	-	-	-	-	-	-	-	0.7	47.6	22
128A	-	-	-	-	-	-	-	-	-	-	-	0.7	104.5	146
128B	-	-	-	-	-	-	-	-	-	-	-	1.2	58.8	14
158C	-	-	-	-	-	-	-	-	-	-	-	0.9	72	33
126A	-	-	-	-	-	-	-	-	-	-	-	0.3	76.9	112
158A	-	-	-	-	-	-	-	-	-	-	-	1.6	-	69
156A	-	-	-	-	-	-	-	-	-	-	-	1.9	65.7	148
130C	.277	<.055	.250	.250	1.75	.388	<.027	<.055	<.055	<.166	<.055	.009	78	192
130A	.538	<.153	.230	<.153	3.0	1.0	<.07	<.153	<.153	<.46	<.153	1.9	59.4	12
130B	.416	<.166	.416	<.166	6.0	1.5	<.08	<.168	<.166	<.50	<.166	1.2	53.4	94
126B	-	-	-	-	-	-	-	-	-	-	-	.05	151.0	71
126B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
126B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
126B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
129A	-	-	-	-	-	-	-	-	-	-	-	1.2	50.2	113
129B	-	-	-	-	-	-	-	-	-	-	-	1.1	65.4	161

TABLE 24

ENGINE DYNAMOMETER TEST OF CONVERTER EQUIPPED ENGINES

Engine Type: 1972 Pontiac 400 CID

Fuel Used: Indolene #15473 - 0.5 cc lead 91 octane

Converter Type: None

Run No.	Air to Fuel Range	Air to Fuel Actual	Test Mode	Spark Timing	Grams/Mile Particulate 1 cfm Filter	Converter Temp.(°F)	Dilution Tube Temp.(°F)	Filter Temp.(°F)	ppm in Exhaust Condensate HCHO	ppm in Exhaust Condensate NH_3
168A	L	16.0	30 mph CS	Std	.0650	-	89.6	97-100	600	-
135A	L	16.0	30 mph CS	Std	.0378	-	98.0	100-	550	31
168B	L	16.0	60 mph CS	Std	.0275	-	114.8	100-102	440	-
170B	S	15.8	30 mph HS	Adv	.0363	-	91.4	100-102	340	-
132A	S	14.6	30 mph HS	Std	.0423	-	93.0	93-97	300	8
170C	S	15.9	30 mph HS	Ret	.0404	-	91.4	99-102	570	-
170A	S	15.8	30 mph CS	Std	.0433	-	89.6	97-100	510	-
176C	S	14.6	60 mph HS	Adv	.0268	-	119	99-102	440	-
176A	S	15.0	60 mph HS	Std	.0239	-	120	103-105	330	-
176B	S	14.8	60 mph HS	Ret	.0255	-	123	100-103	250	-
132B	S	-	Dow Cycle 2	Std	.0390	-	93-134	93-96	370	13
132B	S	-	Dow Cycle 3	Std	.0390	-	-	-	-	-
132B	S	-	Dow Cycle 4	Std	.0390	-	-	-	-	-
132B	S	-	Dow Cycle 5	Std	.0390	-	-	-	-	-
171A	R	12.4	30 mph CS	Std	.0602	-	89.6	97-100	190	-
171B	R	12.3	30 mph HS	Std	.0431	-	89.6	95-102	300	-
136B	R	12.9	60 mph HS	Std	.0299	-	136	98-100	250	-

Spark setting: Adv = Std -10°
Ret = Std +10°

Continuation of Table 24

ANALYSIS OF EXHAUST GAS

	% by Volume				Parts per Million			
Run No.	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x
168A	12.2	3.4	82.6	.64	385	40	1050	-
135A	11.8	6.1	81.2	.02	170	500	450	-
168B	12.8	4.1	81.8	.31	167	40	1400	-
170B	13.0	3.4	82.0	.75	272	33	505	-
132A	12.7	4.3	81.7	.17	175	550	380	-
170C	12.9	3.6	81.8	.83	397	33	1100	-
170A	12.7	3.8	81.7	.95	360	33	810	-
176C	13.1	2.8	82.4	.75	230	23	1800	-
176A	13.0	3.4	82.0	.61	205	23	1150	-
176B	13.4	3.0	82.1	.64	180	13	850	-
132B	12.2	5.6	81.4	.03	150	-	-	-
132B	11.8	5.7	81.2	.37	137	-	-	-
132B	12.5	4.7	81.6	.25	125	-	-	-
132B	11.8	5.7	81.2	.14	145	-	-	-
171A	9.8	1.55	79.8	9.8	775	7	1050	-
171B	10.1	1.6	80.4	6.9	710	15	1100	-
136B	13.0	2.2	82.2	1.57	280	1150	580	-

Continuation of Table 24

ANALYSIS OF EXHAUST PARTICULATE

Run No.	Trace Metals on Millipore Filter (%) Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	Measured in Particulate % Pb Atomic Absorp	% C on Glass Filter	ppm BaP
168A	-	-	-	-	-	-	-	-	-	-	-	6.4	68.4	424
135A	-	-	-	-	-	-	-	-	-	-	-	4.7	-	63
168B	-	-	-	-	-	-	-	-	-	-	-	10.4	41.0	<8
170B	-	-	-	-	-	-	-	-	-	-	-	4.2	66.1	<13
132A	-	-	-	-	-	-	-	-	-	-	-	7.2	-	<11
170C	-	-	-	-	-	-	-	-	-	-	-	5.6	57.4	19
170A	-	-	-	-	-	-	-	-	-	-	-	6.7	57.0	30
176C	-	-	-	-	-	-	-	-	-	-	-	-	-	127
176A	-	-	-	-	-	-	-	-	-	-	-	-	-	98
176B	-	-	-	-	-	-	-	-	-	-	-	-	-	88
132B	-	-	-	-	-	-	-	-	-	-	-	14.4	-	21
132B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
132B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
132B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
171A	-	-	-	-	-	-	-	-	-	-	-	8.4	58.0	615
171B	-	-	-	-	-	-	-	-	-	-	-	12.1	51.0	225
136B	-	-	-	-	-	-	-	-	-	-	-	12.8	32.1	62

g. Standard spark setting gave a higher percentage of larger particles than either advanced or retarded spark.

3. Discussion

This baseline data will have absolute significance only when used as a comparison to the same engine equipped with various converters. However, several interesting points can be noted when looking at the differences in particulate as a function of engine operating conditions.

As noted in the conclusions, low lead fuel seems to give higher particulates than non-leaded. This was also the conclusion of the work done under Contract CPA-22-69-145, and reported by Moran et al. This data is presented graphically in Figures 19, 20, and 21. The amounts of aldehyde and benzo-α-pyrene did not appear to be significantly changed by the use of 0.5 cc leaded fuel. This was not unexpected. A more meaningful comparison will be the levels of these compounds after the use of a converter. This data will be discussed in a later section.

The air/fuel ratio of the engine had an effect on particulate as shown in Figure 19. The important point to note here is that the standard air/fuel ratio did seem to give the lowest particulate. Figures 19, 20, and 21 show the effect of 60 mph versus 30 mph. In almost every instance, regardless of the air/fuel ratio or spark setting, the equivalent 30 mph run was higher in particulate. This may in part be explained by the difference in dilution tube temperature. Although the filter temperature as shown in Tables 23 and 24 was held within 10°F of 100°F, the dilution tube itself was 40-50°F higher at 60 mph than at 30 mph.

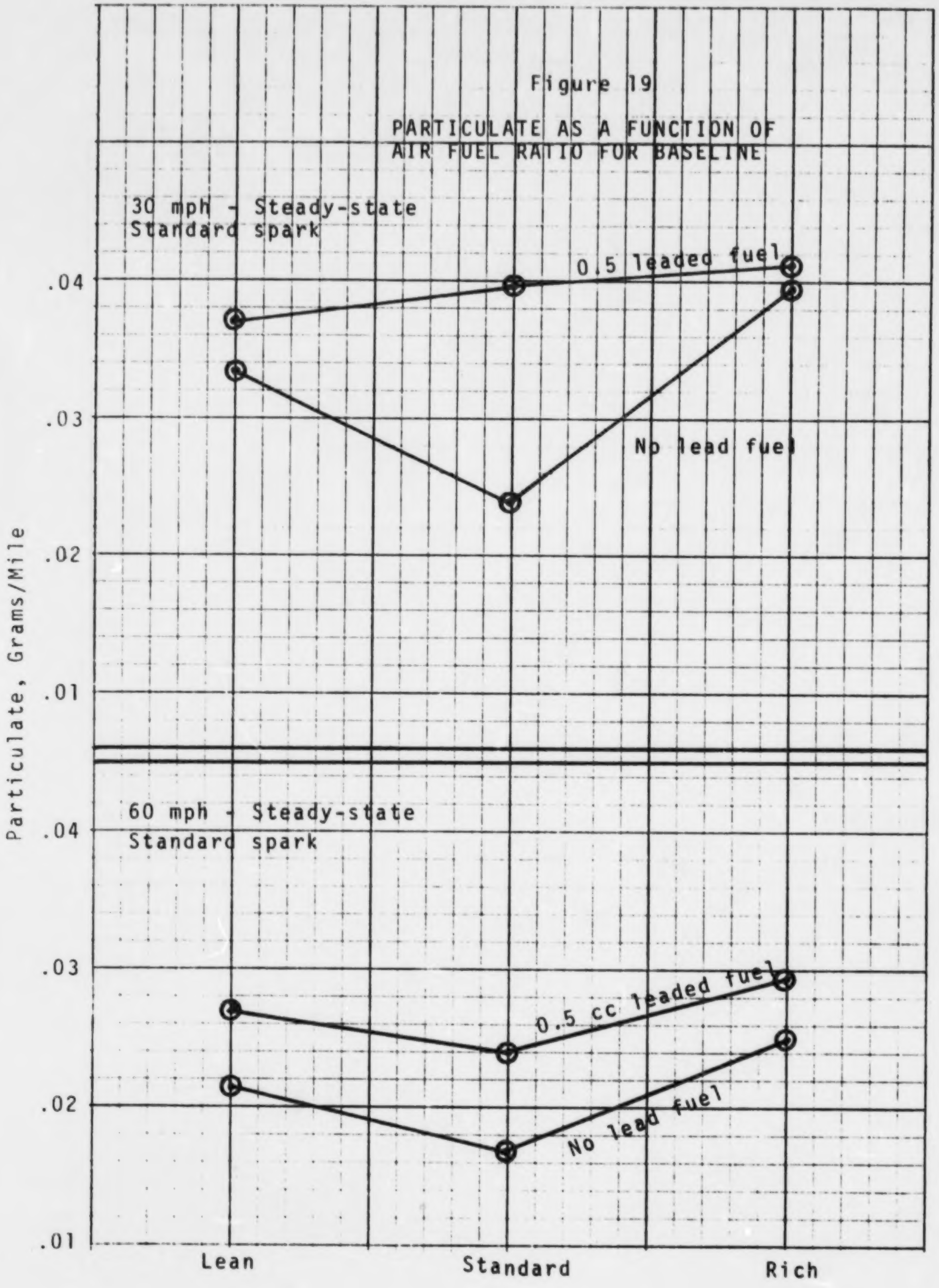


Figure 19

PARTICULATE AS A FUNCTION OF AIR FUEL RATIO FOR BASELINE

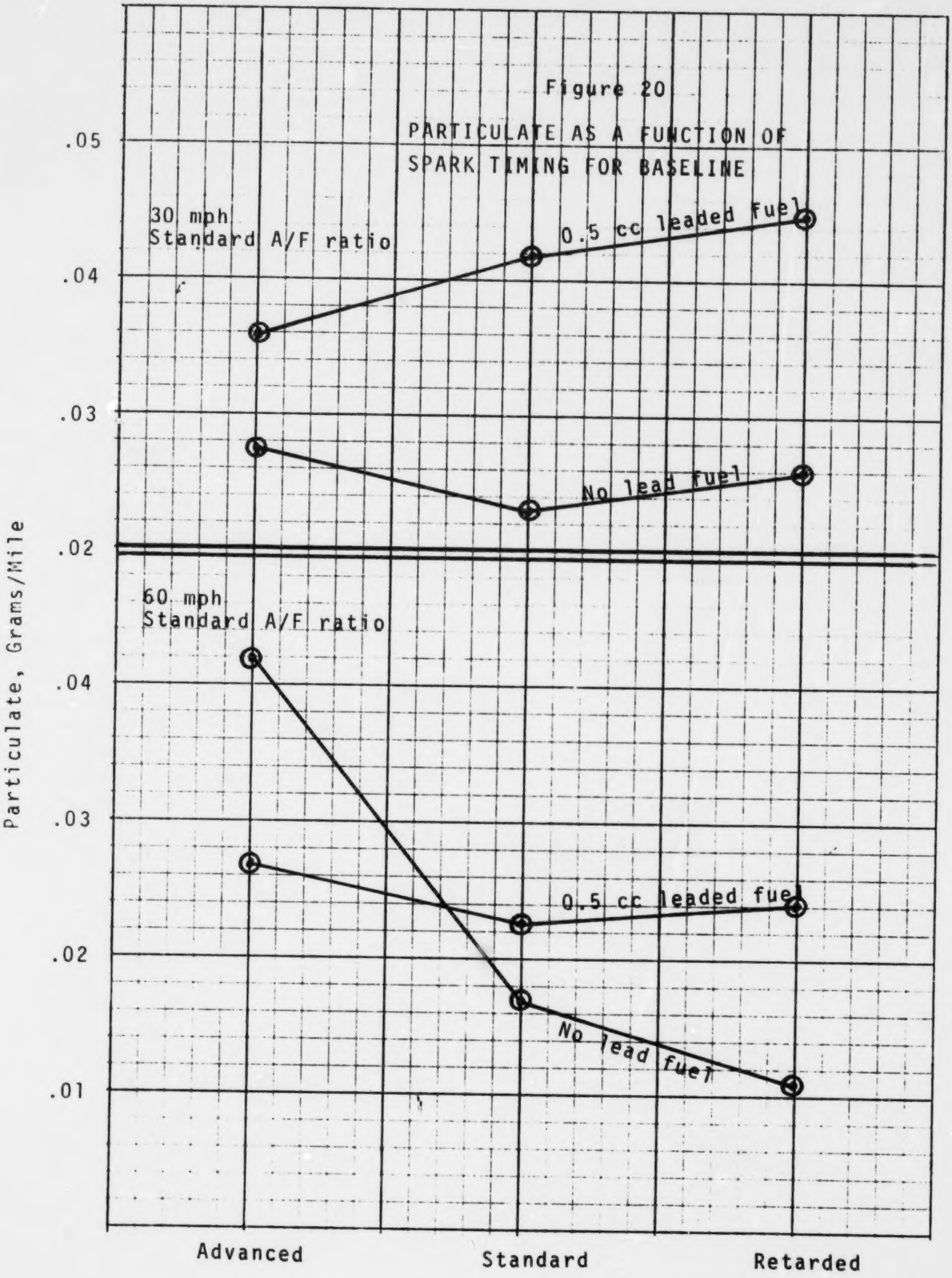


Figure 20

PARTICULATE AS A FUNCTION OF SPARK TIMING FOR BASELINE

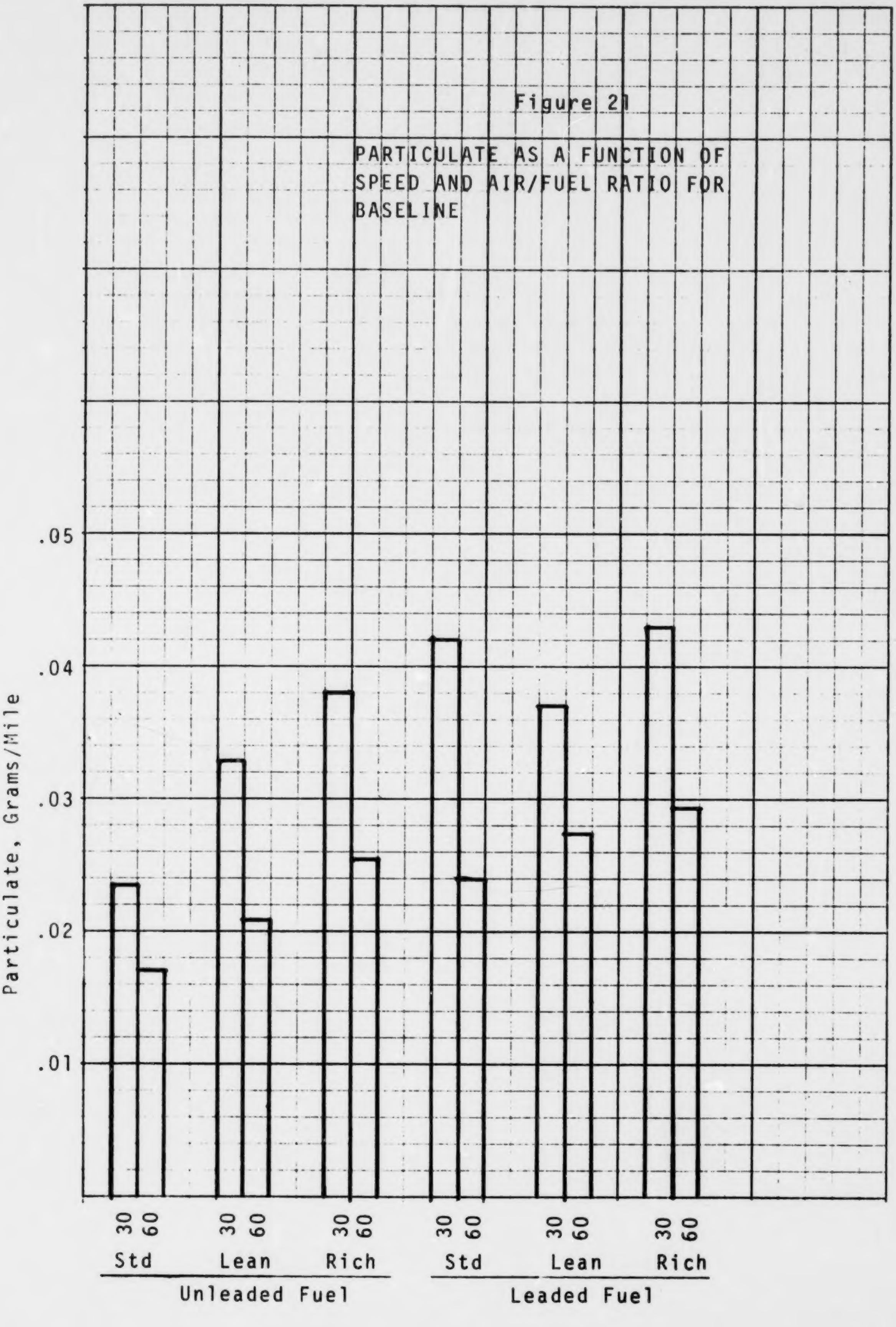


Figure 21

PARTICULATE AS A FUNCTION OF SPEED AND AIR/FUEL RATIO FOR BASELINE

The mass medium equivalent diameter (MMED) can be determined from the mass distribution charts in Figures 22-27. Mass medium equivalent diameter is the diameter of the particle, in microns, of which 50 percent are smaller and 50 percent are larger. The mass distribution plots show the percent of particles less than a given diameter.

In comparing the baseline data with MMED, it is apparent that the standard spark setting gives larger particles than either advanced or retarded spark setting. The MMED for standard spark was approximately 0.6 microns, approximately 0.2 microns for retarded spark, and less than 0.1 for advanced spark. For leaded fuel, at standard spark and standard A/F, the MMED was less than 0.5 microns, which was smaller than that seen with non-leaded fuel.

C. TASK III

1. Introduction

The objective in Task III was to evaluate various emission control devices with respect to their effect on non-regulated emissions. The devices tested under this portion of the contract include:

- Three oxidation catalysts
- One reduction catalyst
- One exhaust gas recirculation system

Initially, work was done using both non-leaded and low lead (0.5 cc/gal) fuel. The leaded fuel itself caused increases in the amount of particulate and, after testing one catalyst on leaded fuel, the rest were run only on non-leaded fuel.

The devices were obtained from either the manufacturer or an automobile company under a secrecy agreement, to protect any proprietary rights involved. Consequently, the data on the

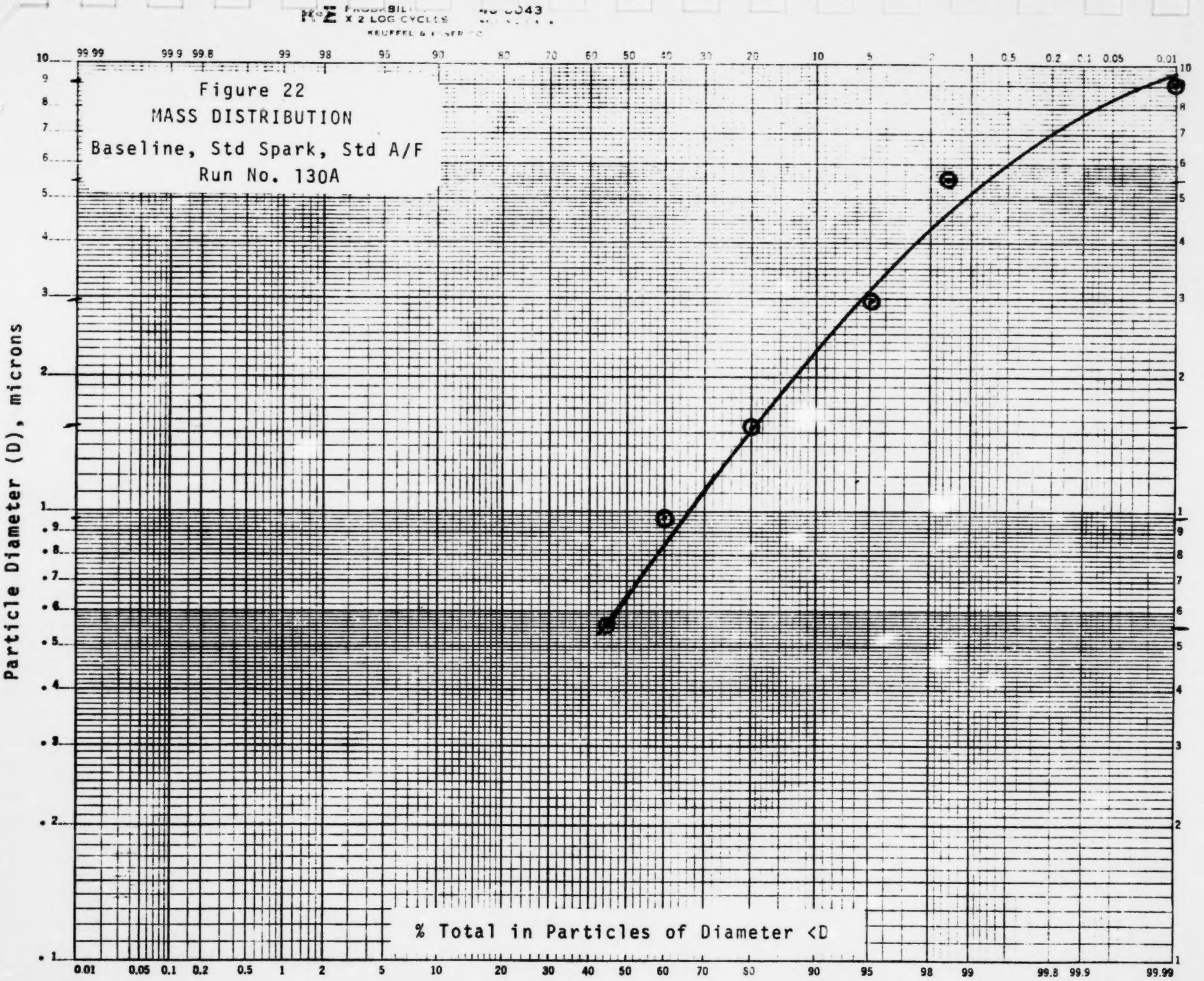


Figure 22
MASS DISTRIBUTION
Baseline, Std Spark, Std A/F
Run No. 130A

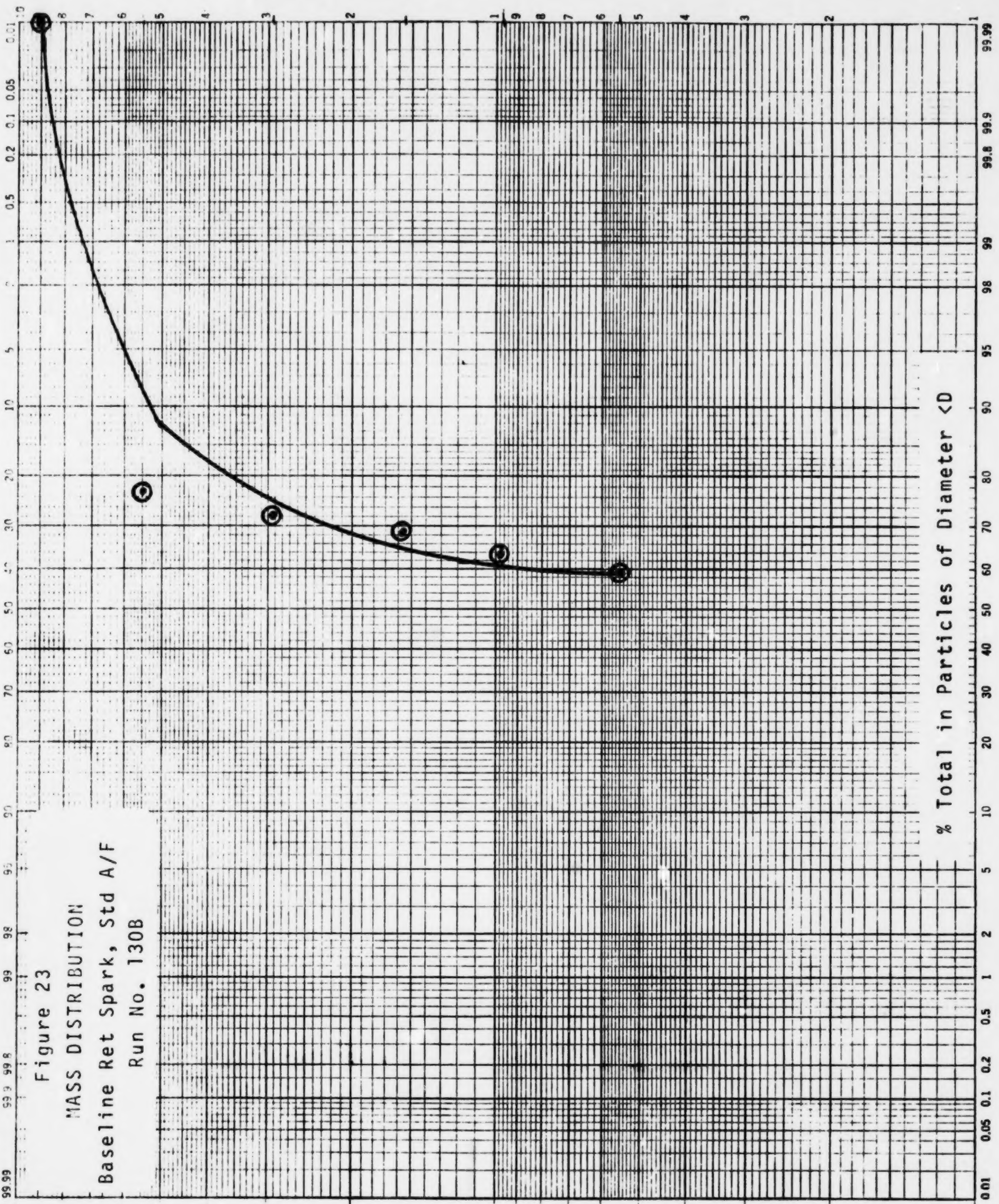


Figure 23
MASS DISTRIBUTION
Baseline Ret Spark, Std A/F
Run No. 130B

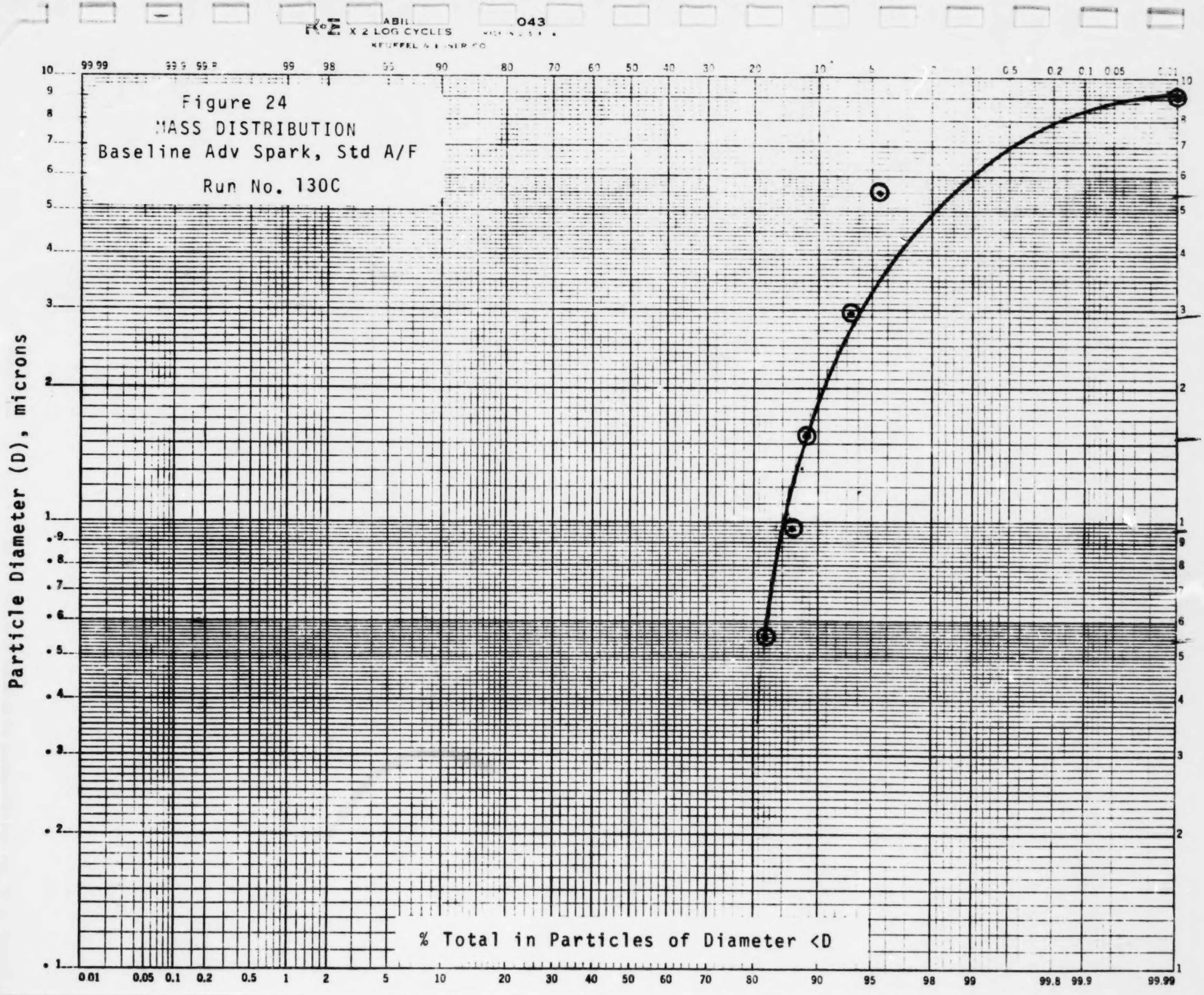


Figure 24
MASS DISTRIBUTION
Baseline Adv Spark, Std A/F

Run No. 130C

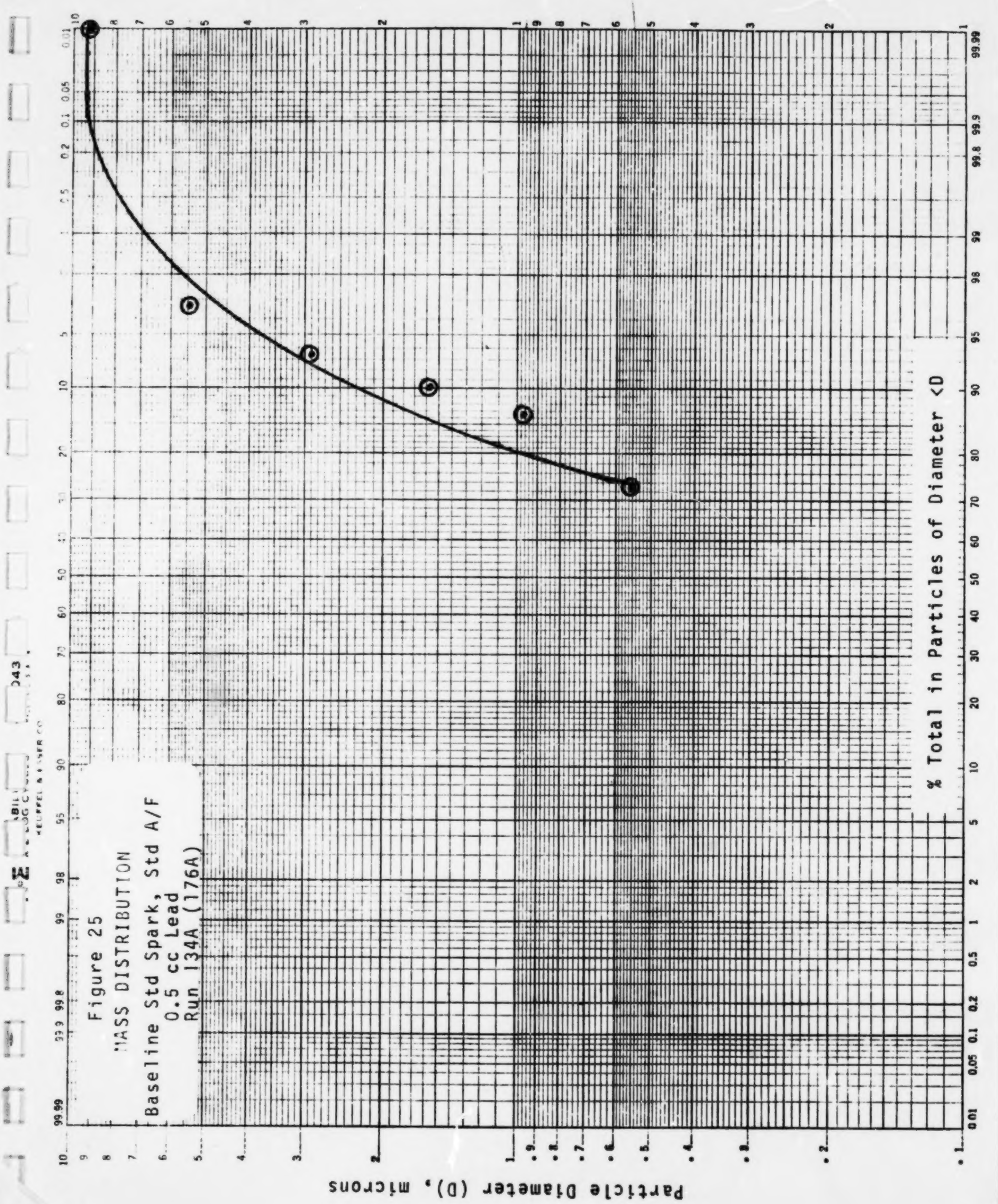


Figure 25
MASS DISTRIBUTION
Baseline Std Spark, Std A/F
0.5 cc Lead
Run 134A (176A)

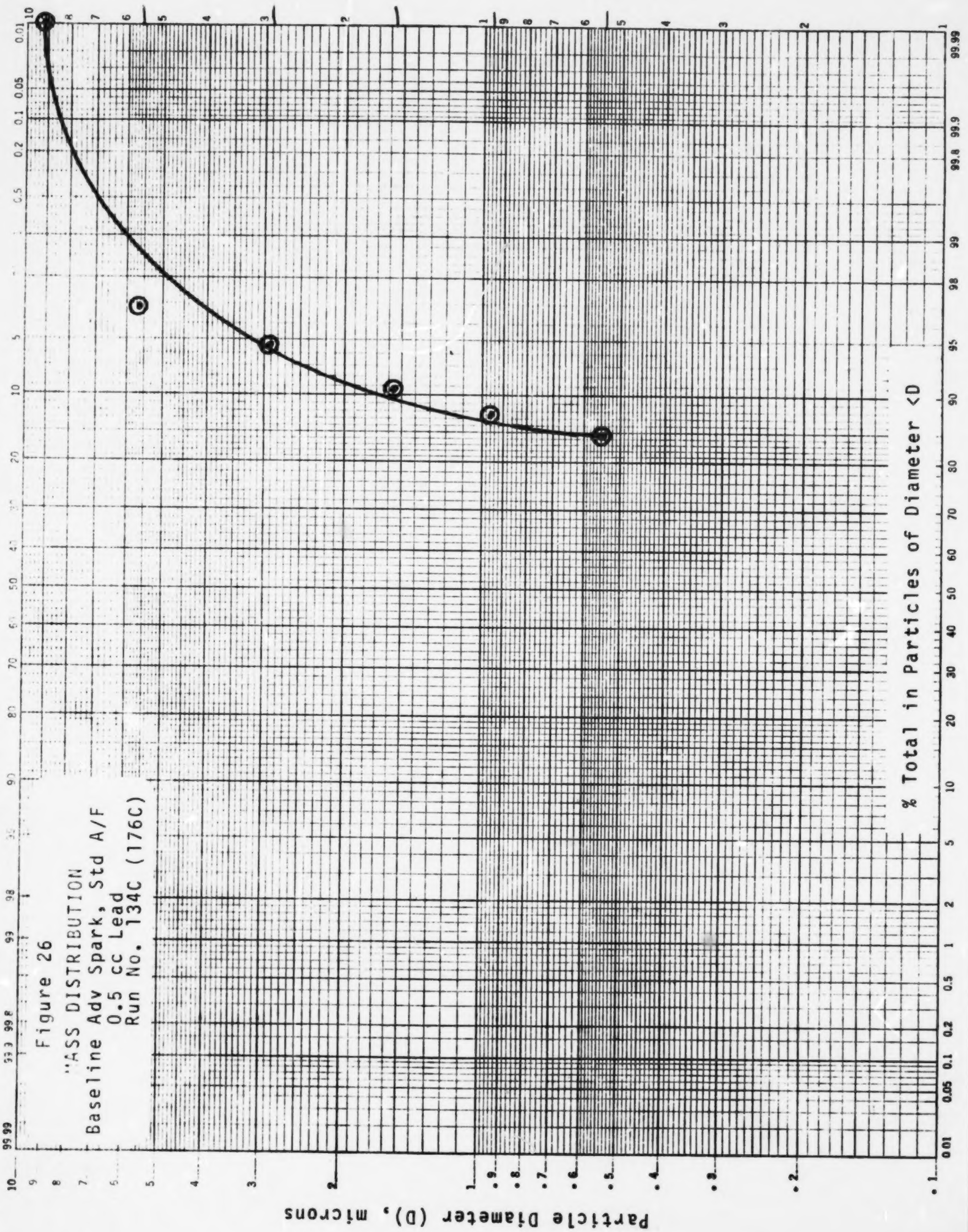


Figure 26

MASS DISTRIBUTION

Baseline Adv Spark, Std A/F

0.5 cc Lead

Run No. 134C (176C)

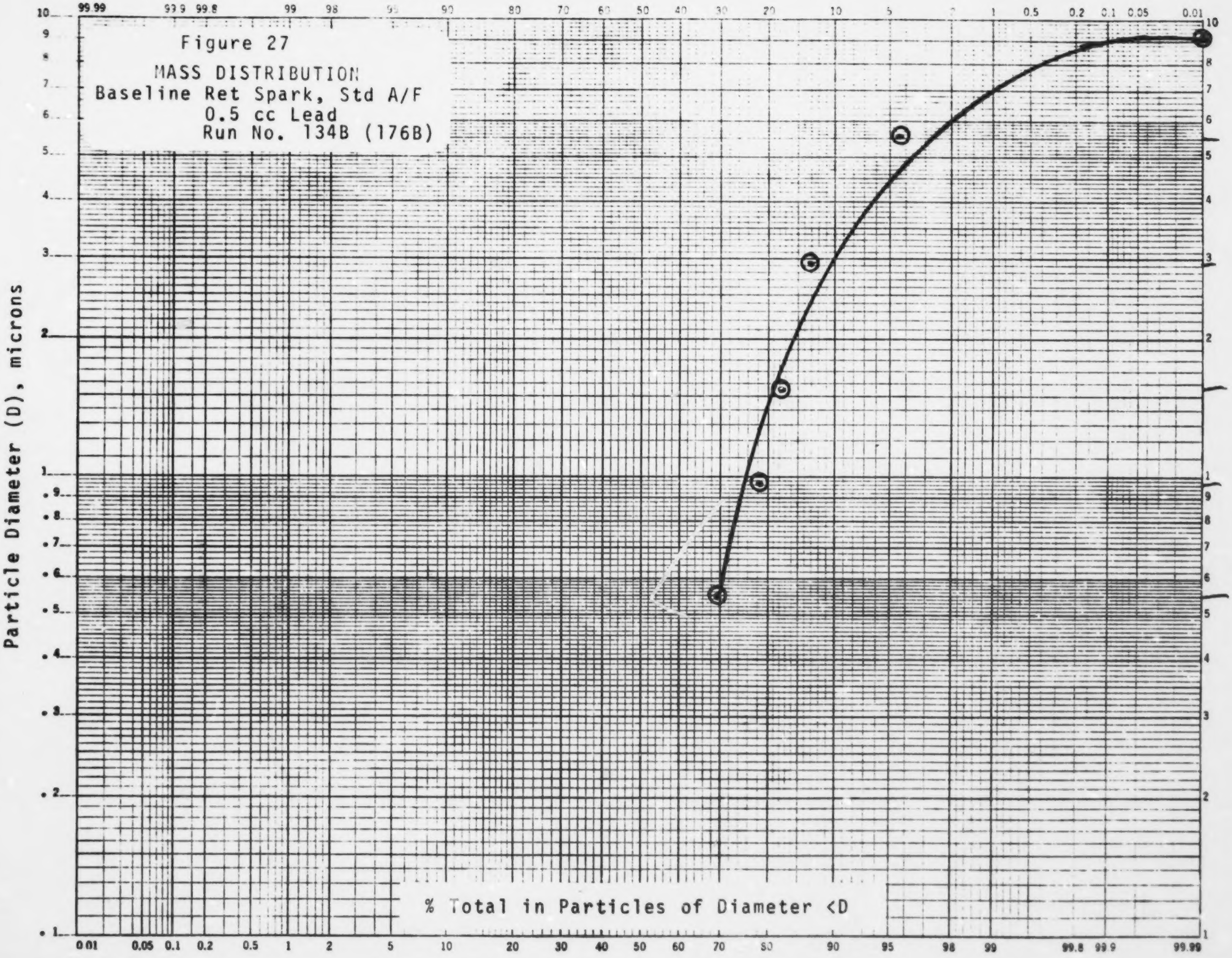


Figure 27

MASS DISTRIBUTION
Baseline Ret Spark, Std A/F
0.5 cc Lead
Run No. 134B (176B)

devices are reported with the only reference to the device being a code letter. The code letters and general description of the devices are as follows:

A. Monolith, noble metal oxidation catalyst
B. Beaded, base metal oxidation catalyst
C. Beaded, base metal oxidation catalyst
D. Monolith reduction catalyst
E. Exhaust gas recirculation system

The data from these runs is shown in Tables 25 -31.

2. Conclusions

a. The use of three different oxidation catalysts on an engine stand, with non-leaded fuel, increased the amounts of particulate collected at 60 mph by a factor of 2-5, compared to a baseline run, except under rich air/fuel ratios. Two catalysts did not generally increase the particulate collected at 30 mph, or under cyclic conditions. The total particulate collected from the control devices was less than normally found when using 3 cc leaded fuel.

b. The three oxidation catalysts significantly lowered the emission of aldehydes, as collected in the condensate.

c. There was no evidence in the particulate of catalyst degradation being the cause of the increase in particulate mass.

d. An increase in particulate comparing 30 mph to 60 mph was noted during the baseline runs. This appeared to be reversed when running at standard conditions with two of the three oxidation catalysts.

TABLE 25

ENGINE DYNAMOMETER TEST OF CONVERTER EQUIPPED ENGINES

Engine Type: 1972 Pontiac 400 CID

Fuel Used: Indolene #15214

Converter Type: "A" with 1975 Hardware, Monolith, Noble Metal

Run No.	Air to Fuel		Test Mode	Spark Timing	Grams/Mile Particulate 1 cfm Filter	Converter Temp. (°F)	Dilution Tube Temp. (°F)	Filter Temp. (°F)	ppm in Exhaust Condensate	
	Range	Actual							HCHO	NH_3
142B	L	15.3	30 mph	Std	.1078	825	87.7	96-100	26	-
142A	L	16.8	60 mph	Std	.1193	1160	127.4	100-102	65	-
143B	S	14.1	30 mph	Std	.0968	865	91.4	98-100	14	-
140C	S	14.2	60 mph	Adv	.0866	1210	131.0	100-102	35	7
140A	S	14.8	60 mph	Std	.0905	1205	131.0	100-102	12	4
140B	S	14.9	60 mph	Ret	.0733	1240	132.8	102-103	7.5	2
143A	S	-	Dow Cycle 2	Std	.0913	820	-	-	29	-
143A	S	-	Dow Cycle 3	Std	.0913	940				
143A	S	-	Dow Cycle 4	Std	.0913	1220				
143A	S	-	Dow Cycle 5	Std	.0913	825				
141B	R	13.1	30 mph	Std	.0092	910	91.4	100-102	9.3	-
141A	R	12.4	60 mph	Std	.0207	1180	131	100-102	71	-

Spark setting: Adv = Std -10°
Ret = Std +10°

Continuation of Table 25

ANALYSIS OF EXHAUST GAS

	Before Converter								After Converter							
	% by Volume				Parts per Million				% by Volume				Parts per Million			
Run No.	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x
142B	11.7	6.2	81.2	.03	165	-	-	-	11.8	6.1	81.2	.03	17	275	590	-
142A	9.9	9.0	80.1	.07	255	-	-	-	11.0	7.3	80.8	.03	35	430	600	-
143B	6.9	13.9	78.3	.07	215	-	-	-	10.5	8.1	80.5	.03	27	450	570	-
140C	12.0	4.6	81.9	.51	215	-	-	-	13.7	2.9	82.5	.03	23	570	850	-
140A	12.3	4.0	82.4	.37	100	-	-	-	13.4	3.3	82.4	.03	14	330	1250	-
140B	12.6	3.7	82.2	.39	61	-	-	-	12.1	5.0	82.0	.03	7	285	850	-
143A	8.4	11.5	79.1	.08	200	-	-	-	10.1	8.9	80.1	.03	30	-	-	-
143A	11.1	7.1	80.8	.04	140	-	-	-	10.0	9.1	80.0	.03	14	-	-	-
143A	11.8	5.6	81.3	.34	130	-	-	-	12.1	5.7	81.4	.03	25	-	-	-
143A	10.8	7.7	80.6	.11	230	-	-	-	9.7	9.2	80.2	.03	39	-	-	-
141B	12.3	4.1	81.7	.82	303	-	-	-	13.7	2.3	81.6	.21	140	200	320	-
141A	12.3	3.5	81.4	2.2	310	-	-	-	12.3	2.3	81.9	2.3	260	390	1650	-

Continuation of Table 25

ANALYSIS OF EXHAUST PARTICULATE

Run No.	Trace Metals on Millipore Filter (%) Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	Measured in Particulate % Pb Atomic Absorp	% C on Glass Filter	ppm BaP
142B	-	-	-	-	-	-	-	-	-	-	-	0.2	<1	<5
142A	-	-	-	-	-	-	-	-	-	-	-	0.2	3.1	21
143B	-	-	-	-	-	-	-	-	-	-	-	0.1	<1	35
140C	-	-	-	-	-	-	-	-	-	-	-	0.1	3.2	6
140A	.06	.02	.09	.05	.60	.10	<.01	<.02	<.02	<.05	<.02	0.2	0.6	17
140B	.09	.02	0.1	.04	.77	.16	<.01	<.02	<.02	<.05	<.02	<0.1	0.4	<3
143A	.08	.02	0.1	.04	.83	.14	<.01	<.02	<.02	<.05	<.02	0.2	1.5	8
143A	-	-	-	-	-	-	-	-	-	-	-	-	-	-
143A	-	-	-	-	-	-	-	-	-	-	-	-	-	-
143A	-	-	-	-	-	-	-	-	-	-	-	-	-	-
141B	-	-	-	-	-	-	-	-	-	-	-	0.2	43.2	<53
141A	-	-	-	-	-	-	-	-	-	-	-	0.9	60.9	17

TABLE 26

ENGINE DYNAMOMETER TEST OF CONVERTER EQUIPPED ENGINES

Engine Type: 1972 Pontiac 400 CID

Fuel Used: Indolene #15473, 0.5 cc lead 91 octane

Converter Type: "A" with 1975 Hardware, Monolith, Noble Metal

Run No.	Air to Fuel Range	Air to Fuel Actual	Test Mode	Spark Timing	Grams/Mile Particulate 1 cfm Filter	Converter Temp. (°F)	Dilution Tube Temp. (°F)	Filter Temp. (°F)	ppm in Exhaust Condensate HCHO	ppm in Exhaust Condensate NH_3
167A	L	16.0	30 mph CS	Std	.0388	910	89.6	99-102	180	-
151B	L	15.4	30 mph HS	Std	.0364	960	93.2	100-104	100	-
151A	L	15.6	60 mph HS	Std	.0742	1250	127.4	100-102	118	-
166C	S	15.1	30 mph HS	Adv	.0256	950	93.2	98-102	110	-
146A	S	14.5	30 mph HS	Std	.0245	920	93.2	98-102	100	-
166B	S	15.1	30 mph HS	Ret	.0222	1000	89.6	99-102	66	-
166A	S	15.2	30 mph CS	Std	.0257	1000	87.0	99-100	170	-
145C	S	15.5	60 mph HS	Adv	.1268	1200	127	100-102	97	6
145A	S	15.6	60 mph HS	Std	.1130	1210	140	100-104	61	2
145B	S	15.6	60 mph HS	Ret	.1001	1260	127	95-97	30	5
146B	S	-	Dow Cycle 2	Std	.0580	800	-	-	100	-
146B	S	-	Dow Cycle 3	Std	.0580	1075				
146B	S	-	Dow Cycle 4	Std	.0580	1240				
146B	S	-	Dow Cycle 5	Std	.0580	870				
165A	R	12.0	30 mph CS	Std	.0592	1150	98.6	102-104	26	-
150A	R	14.2	30 mph HS	Std	.0354	1070	95.0	100-105	72	-
150B	R	13.3	60 mph HS	Std	.0305	1250	129	100-102	<10	-

Spark setting: Adv = Std -10°
Ret = Std +10°

Continuation of Table 26

ANALYSIS OF EXHAUST GAS

	Before Converter								After Converter							
	% by Volume				Parts per Million				% by Volume				Parts per Million			
Run No.	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x
167A	12.7	4.3	81.8	.32	298	-	-	-	13.2	4.15	81.7	.03	75	40	1100	-
151B	9.6	9.2	80.0	.34	260	-	-	-	9.8	9.2	80.1	.03	84	200	500	-
151A	10.9	7.1	80.8	.38	178	-	-	-	8.9	10.4	79.5	.03	40	650	520	-
166C	12.7	4.1	81.6	.52	375	-	-	-	13.6	3.3	82.0	.03	100	33	1100	-
146A	11.5	6.5	81.3	.06	200	-	-	-	11.6	6.3	81.1	.03	75	240	575	-
166B	13.1	3.4	82.0	.64	225	-	-	-	13.9	2.8	82.3	.03	65	33	600	-
166A	12.5	4.0	81.7	.70	315	-	-	-	14.0	2.7	82.3	.03	120	10	850	-
145C	12.2	5.1	81.6	.20	170	-	-	-	11.5	6.5	81.0	.03	37	625	975	-
145A	12.0	5.8	81.2	.11	140	-	-	-	10.6	5.9	81.2	.29	20	555	850	-
145B	11.1	6.8	80.4	.16	175	-	-	-	11.2	6.9	80.9	.03	8	250	690	-
146B	10.8	7.4	80.8	.04	200	-	-	-	-	-	-	-	-	-	-	-
145B	11.9	4.9	81.3	.95	288	-	-	-	-	-	-	-	-	-	-	-
146B	11.4	6.3	80.9	.38	190	-	-	-	-	-	-	-	-	-	-	-
145B	11.0	7.3	80.8	.06	165	-	-	-	-	-	-	-	-	-	-	-
165A	11.4	2.6	81.0	3.9	496	-	-	-	13.2	0.6	82.6	2.78	480	40	900	-
150A	8.0	11.5	79.0	.61	280	-	-	-	9.9	9.2	80.0	.06	145	240	450	-
150B	10.8	4.8	80.7	2.79	425	-	-	-	10.9	6.4	80.9	.86	220	460	930	-

Continuation of Table 26

ANALYSIS OF EXHAUST PARTICULATE

Run No.	Trace Metals on Millipore Filter (%)											Measured in Particulate		
	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	% Pb Atomic Absorp	% C on Glass Filter	ppm BaP
167A	-	-	-	-	-	-	-	-	-	-	-	1.4	7.3	90
151B	-	-	-	-	-	-	-	-	-	-	-	0.9	12.1	19
151A	-	-	-	-	-	-	-	-	-	-	-	0.9	12.3	22
166C	-	-	-	-	-	-	-	-	-	-	-	2.5	12.0	<19
146A	-	-	-	-	-	-	-	-	-	-	-	1.8	5.3	-
166B	-	-	-	-	-	-	-	-	-	-	-	2.3	8.3	<21
166A	-	-	-	-	-	-	-	-	-	-	-	2.5	20	62
145C	.036	<.007	.056	.020	.40	.040	<.004	<.007	<.007	<.020	<.007	0.7	3.9	<<4
145A	.075	<.008	.058	.026	.41	.052	<.004	.015	<.008	<.021	<.008	0.7	3.1	<4
145B	2.9	<.05	3.2	.90	.21	2.2	<.25	.53	.50	<1.5	<.50	0.7	3.9	-
146B	-	-	-	-	-	-	-	-	-	-	-	1.5	3.4	<6
146B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
146B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
146B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
165A	-	-	-	-	-	-	-	-	-	-	-	11.9	41.2	374
150A	-	-	-	-	-	-	-	-	-	-	-	-	20.4	<13
150B	-	-	-	-	-	-	-	-	-	-	-	-	20.2	24

TABLE 27

ENGINE DYNAMOMETER TEST OF CONVERTER EQUIPPED ENGINES

Engine Type: 1972 Pontiac 400 CID

Fuel Used: Indolene #15214, No lead 91 octane

Converter Type: "B" with 1975 Hardware, Beaded, Base Metal

Run No.	Air to Fuel		Test Mode	Spark Timing	Grams/Mile Particulate 1 cfm Filter	Converter Temp. (°F)	Dilution Tube Temp. (°F)	Filter Temp. (°F)	ppm in Exhaust Condensate	
	Range	Actual							HCHO	NH_3
183A	L	16.6	60 mph	Std	.1165	1140	129	102-105	3.8	1.0
182B	S	15.4	60 mph	Ret	.1134	1200	129	104-107	2.1	3.0
181A	S	14.9	30 mph	Std	.0048	795	92	100-104	19	36
181C	S	15.2	60 mph	Std	.1052	1235	131	103-106	5.9	7
182A	S	-	Dow Cycle 2	Std	.0256	825	112	99-100	6.5	10.0
182A	S	-	Dow Cycle 3	Std	.0256	1100				
182A	S	-	Dow Cycle 4	Std	.0256	1190				
182A	S	-	Dow Cycle 5	Std	.0256	975				
180A	R	-	30 mph	Std	Nil	950	89	99-103	6.0	87
179A	R	13.7	60 mph	Std	.0522	1290	130	104-107	3.5	35
179B	R	13.8	60 mph	Std	.0183	1235	122	98-100	0.7	1700

Spark setting: Adv = Std -10°
Ret = Std +10°

Continuation of Table 27

ANALYSIS OF EXHAUST GAS

	Before Converter								After Converter							
	% by Volume				Parts per Million				% by Volume				Parts per Million			
Run No.	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x
183A	11.2	7.0	80.9	.03	40	-	-	-	11.4	6.7	80.9	.03	5	85	500	-
182B	12.5	4.7	81.7	.03	25	-	-	-	12.8	4.3	81.9	.03	5	55	975	-
181A	12.0	5.7	81.4	.03	150	-	-	-	12.4	5.2	81.5	.03	40	-	-	-
181C	12.7	3.8	82.0	.27	40	-	-	-	13.1	3.3	82.2	.03	5	65	1600	-
182A	12.5	4.8	81.7	.08	180	-	-	-	13.0	4.3	81.8	.03	35	-	-	-
182A	12.7	4.7	81.5	.15	125	-	-	-	13.1	4.0	81.4	.03	25	65	920	-
182A	12.5	5.8	81.6	.03	65	-	-	-	13.0	4.2	81.8	.03	10	75	1800	-
182A	12.3	5.1	81.6	.06	160	-	-	-	13.0	4.1	81.9	.03	10	72	1000	-
180A	14.5	0.9	82.9	.79	350	-	-	-	14.9	0.4	83.2	.55	150	7	930	-
179A	12.9	3.4	81.9	.03	50	-	-	-	14.8	2.5	81.6	.03	8	37	1500	-
179B	14.4	1.1	82.7	.03	220	-	-	-	15.1	0.5	82.8	.40	90	17	1600	-

Continuation of Table 27

ANALYSIS OF EXHAUST PARTICULATE

Run	Trace Metals on Millipore Filter (%)											Measured in Particulate		
No.	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	% Pb Atomic Absorp	% C on Glass Filter	ppm BaP
183A	-	-	-	-	-	-	-	-	-	-	-	-	5.0	4
182B	-	-	-	-	-	-	-	-	-	-	-	-	5.1	24
181A	-	-	-	-	-	-	-	-	-	-	-	-	7.9	145
181C	.21	.016	.050	.240	.240	.055	<.008	<.008	<.008	.058	<.008	-	2.9	10
182A	-	-	-	-	-	-	-	-	-	-	-	-	48.5	-
182A	-	-	-	-	-	-	-	-	-	-	-	-	-	-
182A	-	-	-	-	-	-	-	-	-	-	-	-	-	-
182A	-	-	-	-	-	-	-	-	-	-	-	-	-	-
180A	-	-	-	-	-	-	-	-	-	-	-	-	-	11
179A	-	-	-	-	-	-	-	-	-	-	-	-	<.5	39
179B	-	-	-	-	-	-	-	-	-	-	-	-	<.5	-

TABLE 28

ENGINE DYNAMOMETER TEST OF CONVERTER EQUIPPED ENGINES

Engine Type: 1972 Pontiac 400 CID

Fuel Used: Indolene #15214, No lead 91 octane

Converter Type: "C" with 1975 Hardware, Beaded, Base Metal

Run No.	Air to Fuel		Test Mode	Spark Timing	Grams/Mile Particulate 1 cfm Filter	Converter Temp.(°F)	Dilution Tube Temp.(°F)	Filter Temp.(°F)	ppm in Exhaust Condensate		ppm in Exhaust Gas	
	Range	Actual							HCHO	NH_3	HCHO	NH_3
184A	L	16.6	60 mph	Std	.0052	1140	134	107-110	0.8	3.4	0.023	0.18
185A	S	14.9	60 mph	Ret	.0533	1190	126	105-107	0.3	1.0	0.009	0.06
186B	S	15.0	30 mph	Std	Nil	810	92.0	104-105	28	3.9	0.95	0.23
186A	S	14.7	60 mph	Std	.0554	1150	125	104-105	5.3	1.2	0.17	0.068
185B	S	14.5	Dow Cycle 2	Std	.0383	750	115	106-107	4.8	3.2	-	-
185B	S	14.7	Dow Cycle 3	Std	.0383	975						
185B	S	14.8	Dow Cycle 4	Std	.0383	1175						
185B	S	14.8	Dow Cycle 5	Std	.0383	840						
187C	R	13.4	30 mph	Std	.0117	875	95.0	103-105	1.5	740.0	0.068	38.8
187B	R	13.4	60 mph	Std	.0360	1440	142	109-112	0.2	15.3	0.006	0.88
187A	R	13.3	60 mph	Std	.0171	1175	115	100-101	0.2	2180.0	0.008	154.66

Continuation of Table 28

ANALYSIS OF EXHAUST GAS

	Before Converter								After Converter							
	% by Volume				Parts per Million				% by Volume				Parts per Million			
Run No.	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x
184A	12.0	5.5	81.6	.03	45	-	-	-	12.5	4.6	81.6	.03	1	93	1500	-
185A	12.8	4.4	81.8	.03	20	-	-	-	13.2	4.1	81.8	.03	1	33	1000	-
186B	12.2	5.2	81.6	.10	142	-	-	-	12.5	4.8	81.8	.03	37.5	7	1100	-
186A	12.6	4.8	81.7	.03	45	-	-	-	13.1	4.1	81.9	.03	1	65	1500	-
185B	12.4	4.8	81.8	.32	160	-	-	-	12.7	4.7	81.7	.03	10	8	900	-
185B	11.8	5.9	81.3	.11	90	-	-	-	12.3	5.3	81.5	.03	10	58	900	-
185B	12.9	4.1	82.0	.09	50	-	-	-	13.1	3.9	82.1	.03	2	65	1850	-
185B	12.2	5.2	81.6	.03	170	-	-	-	12.4	5.0	81.5	.03	1	33	1000	-
187C	14.3	1.0	82.7	.06	250	-	-	-	15.0	0.35	83.1	.41	132	15	560	-
187B	13.1	2.3	82.5	.95	65	-	-	-	14.9	1.2	83.0	.03	5	10	425	-
187A	14.2	0.7	82.5	.53	226	-	-	-	15.1	0.27	83.0	.20	135	8	380	-

Continuation of Table 28

ANALYSIS OF EXHAUST PARTICULATE

Run No.	Trace Metals on Millipore Filter (%)											Measured in Particulate		
	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	% Pb Atomic Absorp	% C on Glass Filter	ppm BaP
184A	-	-	-	-	-	-	-	-	-	-	-	-	57.9	36
185A	-	-	-	-	-	-	-	-	-	-	-	-	7.6	13
186B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
186A	.21	<.024	.16	.093	.98	.25	<.024	.057	.045	.086	.024	-	11.1	16
185B	-	-	-	-	-	-	-	-	-	-	-	-	31.6	<9
185B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
185B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
185B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
187C	-	-	-	-	-	-	-	-	-	-	-	-	91.0	145
187B	-	-	-	-	-	-	-	-	-	-	-	-	20.0	36
187A	-	-	-	-	-	-	-	-	-	-	-	-	43.4	<13

TABLE 29
ENGINE DYNAMOMETER TEST OF CONVERTER EQUIPPED ENGINES

Engine Type: 1972 Pontiac 400 CID
Fuel Used: Indolene #15214, No lead 91 octane
Converter Type: NO_x - "D", Monolith

Run No.	Air to Fuel		Test Mode	Spark Timing	Grams/Mile Particulate 1 cfm Filter	Converter Temp. (°F)	Dilution Tube Temp. (°F)	Filter Temp. (°F)	ppm in Exhaust Condensate		ppm in Exhaust Gas	
	Range	Actual							HCHO	NH_3	HCHO	NH_3
201A	R	13.9	60 mph	Std	.0052	1090	125	104-107	33	310	1.27	23.3
202A	R	13.9	60 mph	Std	.0126	1100	111	98-100	32	320	1.33	23.5
202B	R	13.8	60 mph	Adv	.0129	1105	113	97-99	13	-	0.600	-
202C	R	13.8	60 mph	Rtd	.0036	-	-	-	13	-	0.62	-
202D	R	13.8	30 mph	Std	.0031	-	-	-	-	-	-	-

Spark setting: Adv = Std -10°
Ret = Std +10°

Continuation of Table 29

ANALYSIS OF EXHAUST GAS

Run No.	Before Converter								After Converter							
	% by Volume				Parts per Million				% by Volume				Parts per Million			
	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x
201A	13.7	0.9	82.8	1.63	250	7	1400	-	13.8	0.7	83.0	1.5	220	7	1050	-
202A	14.0	0.73	83.2	1.16	240	16	1600	-	14.1	0.56	83.6	0.72	200	5	1150	-
202B	13.3	0.75	83.8	1.11	250	10	1750	-	13.7	0.6	84.1	0.67	170	10	1100	-

TABLE 30

ENGINE DYNAMOMETER TEST OF CONVERTER EQUIPPED ENGINES

Engine Type: 1972 Pontiac 400 CID

Fuel Used: Indolene #15214, No lead 91 octane

Converter Type: EGR - ON-

Run No.	Air to Fuel		Test Mode	Spark Timing	Grams/Mile Particulate 1 cfm Filter	Converter Temp. (°F)	Dilution Tube Temp. (°F)	Filter Temp. (°F)	ppm in Exhaust Condensate		ppm in Exhaust Gas	
	Range	Actual							HCHO	NH_3	HCHO	NH_3
228G	L	16.7	60 mph	Std	.0124	-	185	100-120	460.46	41.25	21.0	3.3
228F	S	15.0	60 mph	Ret	.0071	-	210	125-130	108.9	4.9	5.2	0.4
228A	S	15.7	30 mph	Std	.0314	-	109	92-98	569.2	35.9	31.4	3.5
228B	S	15.6	60 mph	Std	.0097	-	185	110-118	342.8	29.9	7.5	1.2
228C	S	15.3	Dow Cycle 2	Std	.0183	-	95-215	100-125	889.6	12.7	-	-
228C	S	15.3	Dow Cycle 3	Std	-	-						
228C	S	15.3	Dow Cycle 4	Std	-	-						
228C	S	15.3	Dow Cycle 5	Std	-	-						
228E	R	13.5	30 mph	Std	.0227	-		85-90	461.9	15.4	41.9	2.4
228D	R	13.5	60 mph	Std	.0079	-		225-245	282.44	20.4	27.1	3.4

Spark setting: Adv = Std -10°
Ret = Std +10°

Continuation of Table 30

EXHAUST GAS ANALYSIS

% by Volume				Parts per Million			
CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x
14.4	7.3	80.3	.03	80	65	600	-
12.4	4.8	81.7	.03	40	45	650	-
10.9	6.8	81.2	.03	206	50	100	-
11.4	6.0	81.6	.03	110	65	1000	-
11.3	6.6	81.3	.03	160	48	200	-
11.7	5.6	81.3	.03	135	48	600	-
11.9	5.4	81.6	.03	75	72	1220	-
11.4	6.5	81.2	.03	135	48	275	-
11.6	4.9	81.2	1.20	175	30	150	-
12.4	2.7	82.2	1.67	75	32	940	-

Continuation of Table 30

ANALYSIS OF EXHAUST PARTICULATE

Run	Trace Metals on Millipore Filter (%)											Measured in Particulate		
No.	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	% Pb Atomic Absorp	% C on Glass Filter	ppm BaP
228G	-	-	-	-	-	-	-	-	-	-	-	-	36.7	21
228G	-	-	-	-	-	-	-	-	-	-	-	-	49.8	33
228A	-	-	-	-	-	-	-	-	-	-	-	-	55.6	120
228B	14	<2	8	10	54	14	<2	<2	<2	14	<2	-	47.3	28
228C	-	-	-	-	-	-	-	-	-	-	-	-	50.8	68
228C	-	-	-	-	-	-	-	-	-	-	-	-	-	-
228C	-	-	-	-	-	-	-	-	-	-	-	-	-	-
228C	-	-	-	-	-	-	-	-	-	-	-	-	-	-
228E	-	-	-	-	-	-	-	-	-	-	-	-	46.0	230
228D	-	-	-	-	-	-	-	-	-	-	-	-	46.4	120

TABLE 31

ENGINE DYNAMOMETER TEST OF CONVERTER EQUIPPED ENGINES

Engine Type:	1972 Pontiac 400 CID
Fuel Used:	Indolene #15214, No lead 91 octane
Converter Type:	EGR - Off

Run No.	Air to Fuel Range	Air to Fuel Actual	Test Mode	Spark Timing	Grams/Mile Particulate 1 cfm Filter	Converter Temp. (°F)	Dilution Tube Temp. (°F)	Filter Temp. (°F)	ppm in Exhaust Condensate HCHO	ppm in Exhaust Condensate NH_3	ppm in Exhaust Gas HCHO	ppm in Exhaust Gas NH_3
229A	L	16.7	60 mph	Std	.0019	-	185	110-120	398.85	32.6	12.8	1.8
229D	S	15.0	60 mph	Ret	.0087	-	200	110-125	146.5	38.2	6.4	2.9
229F	S	15.7	30 mph	Std	.0021	-	105	85-90	518.6	41.1	20.8	2.9
229C	S	15.6	60 mph	Std	.0105	-	195	120-130	40.6	60.3	18.9	4.9
229E	S	15.3	Dow Cycle 2	Std	.0208	-	100-230	110-130	529.2	23.2	-	-
229E	-	-	Dow Cycle 3	Std		-						
229E	-	-	Dow Cycle 4	Std		-						
229E	-	-	Dow Cycle 5	Std		-						
229G	R	13.5	30 mph	Std	.0231	-	110	90-95	406.2	16.0	-	-
229B	R	13.5	60 mph	Std	.0056	-	225	120-140	89.2	62.5	5.1	6.3

Spark setting: Adv = Std -10°
Ret = Std +10°

Continuation of Table 31

ANALYSIS OF EXHAUST GAS

	% by Volume				Parts per Million			
Run No.	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x
229A	11.3	6.3	81.6	.03	75	100	1400	-
229D	17.2	4.8	81.6	.53	55	72	1400	-
229F	11.5	6.3	81.3	.03	120	50	950	-
229C	11.9	5.0	81.3	.83	75	80	2000	-
229E	11.7	5.8	81.4	.03	130	55	850	-
229E	11.7	5.1	82.2	.03	100	55	1100	-
229E	12.2	4.5	82.3	.03	95	120	2500	-
229E	11.6	5.8	81.6	.03	120	55	1000	-
229G	11.0	5.2	81.9	1.05	200	10	650	-
229B	12.9	2.5	81.8	1.86	45	30	1100	-

Continuation of Table 31

ANALYSIS OF EXHAUST PARTICULATE

	Trace Metals on Millipore Filter (%)											Measured in Particulate		
Run No.	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	% Pb Atomic Absorp	% C on Glass Filter	ppm BaP
229A	-	-	-	-	-	-	-	-	-	-	-	-	0.9	<13
229D	-	-	-	-	-	-	-	-	-	-	-	-	0.5	<17
229F	-	-	-	-	-	-	-	-	-	-	-	-	0.8	<17
229C	12	<2	14	4	54	12	<2	<2	<2	10	<2	-	2.7	21
229E	-	-	-	-	-	-	-	-	-	-	-	-	1.2	39
229E	-	-	-	-	-	-	-	-	-	-	-	-	-	-
229E	-	-	-	-	-	-	-	-	-	-	-	-	-	-
229E	-	-	-	-	-	-	-	-	-	-	-	-	-	-
229G	-	-	-	-	-	-	-	-	-	-	-	-	1.3	48
229B	-	-	-	-	-	-	-	-	-	-	-	-	3.0	<24

e. The mass medium equivalent diameter was shifted significantly toward smaller particles, when compared to the baseline, for all of the devices tested.

3. Discussion

The converters tested seemed to have a definite effect on particulate in several ways. First, as mentioned in the conclusions, the three oxidation catalysts all showed higher grams/mile of particulate mass at 60 mph than did the baseline. This is shown graphically in Figure 28. At standard air/fuel ratio, the increase of particulate mass was significant. As the engine was operated richer, however, the difference became small enough to be considered less significant, although real.

The effect at 30 mph showed a reversal of the 60 mph effect for two of the three oxidation catalysts. The two which show a reduced particulate emission at 30 mph (Figure 29) are both base metal beaded catalysts. The EGR system, (Converter E), showed an increase at 30 mph, but was unchanged at 60 mph compared to its own baseline. It is perhaps significant that the same engine, when modified for EGR, showed a decrease in particulate mass compared to the previous baseline.

The particulate mass collected during the Dow cycle (Table 2) for the various converters showed little significant change, although Converter A was quite high. This data is shown graphically in Figure 30.

The increase noted in the particulate mass when using the oxidation catalysts was not accounted for by anything which was routinely measured as part of this contract.

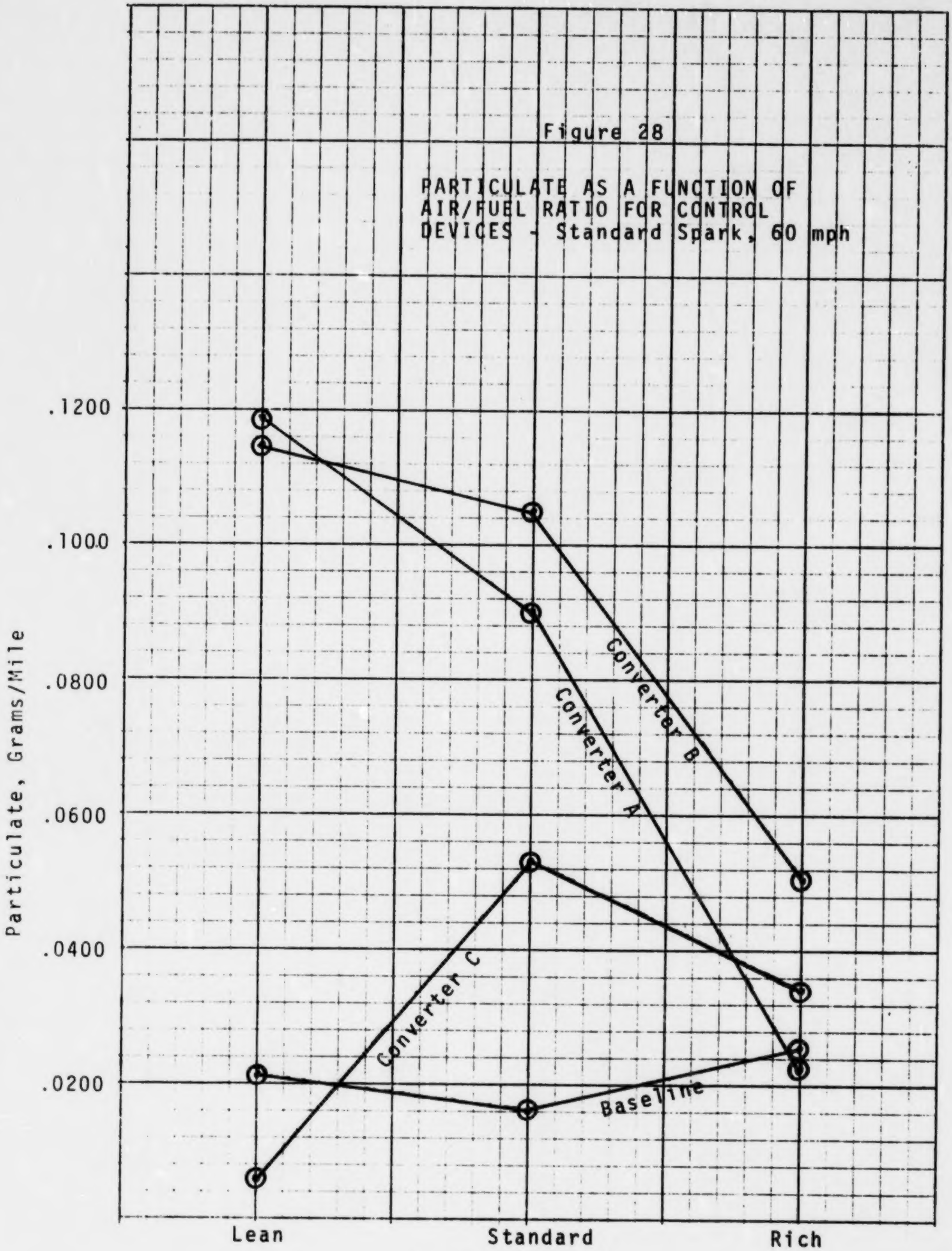


Figure 28

PARTICULATE AS A FUNCTION OF
AIR/FUEL RATIO FOR CONTROL
DEVICES - Standard Spark, 60 mph

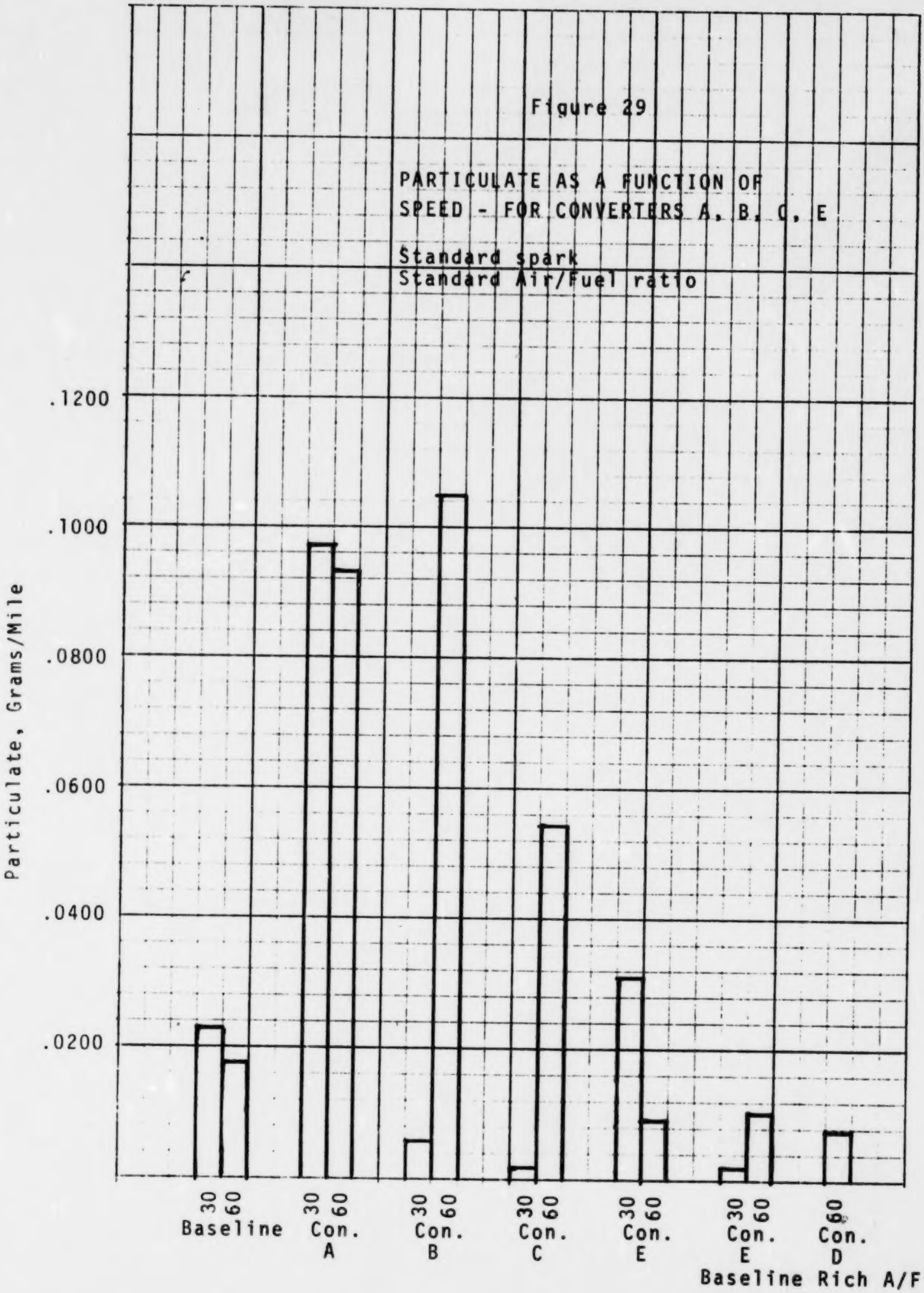
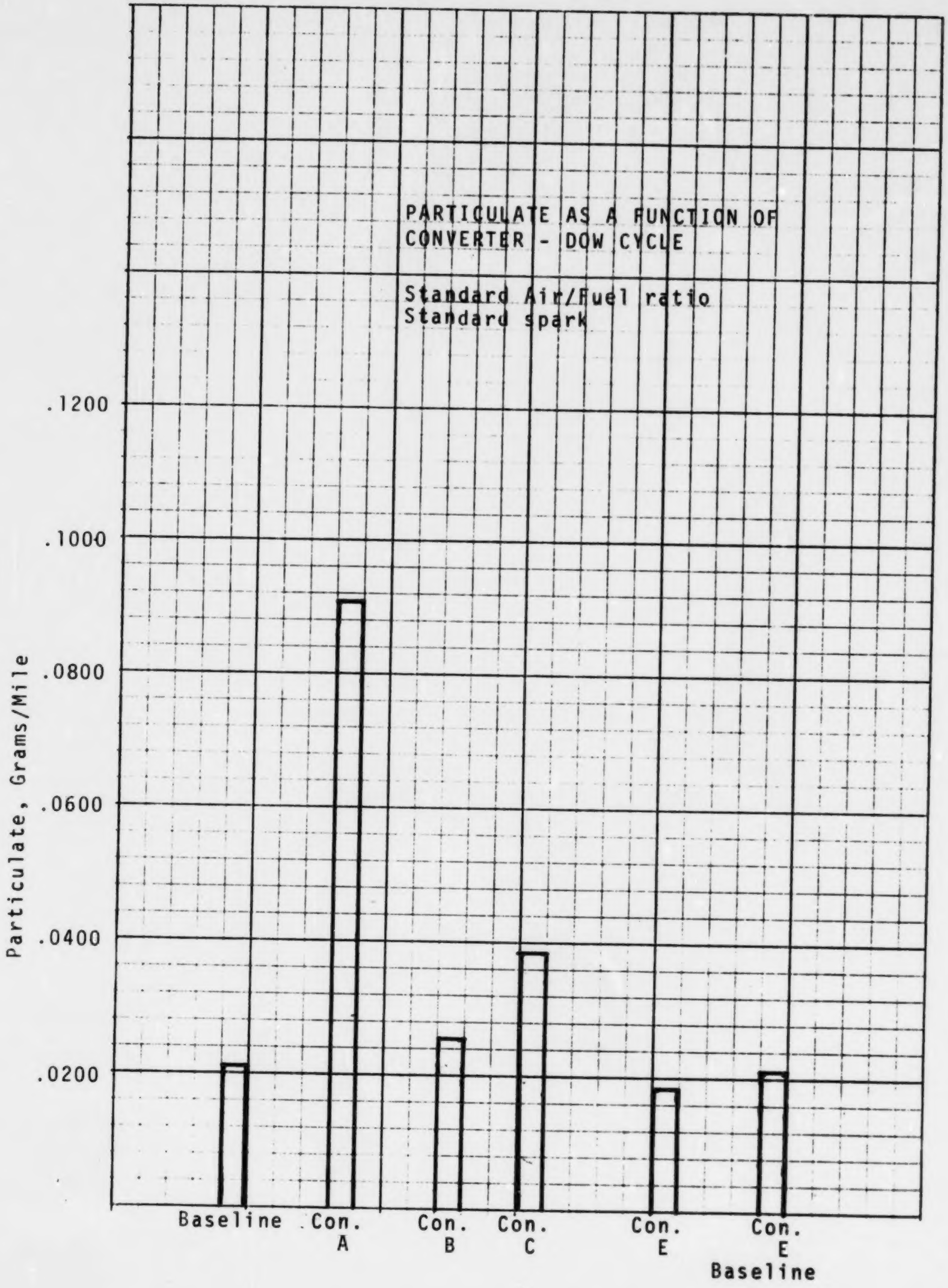


Figure 29

PARTICULATE AS A FUNCTION OF SPEED - FOR CONVERTERS A, B, C, E

Standard spark
Standard Air/Fuel ratio


PARTICULATE AS A FUNCTION OF CONVERTER - DOW CYCLE
Standard Air/Fuel ratio
Standard spark
Particulate, Grams/Mile
.1200
.1000
.0800
.0600
.0400
.0200
Baseline
Con. A
Con. B
Con. C
Con. E
Con. E Baseline

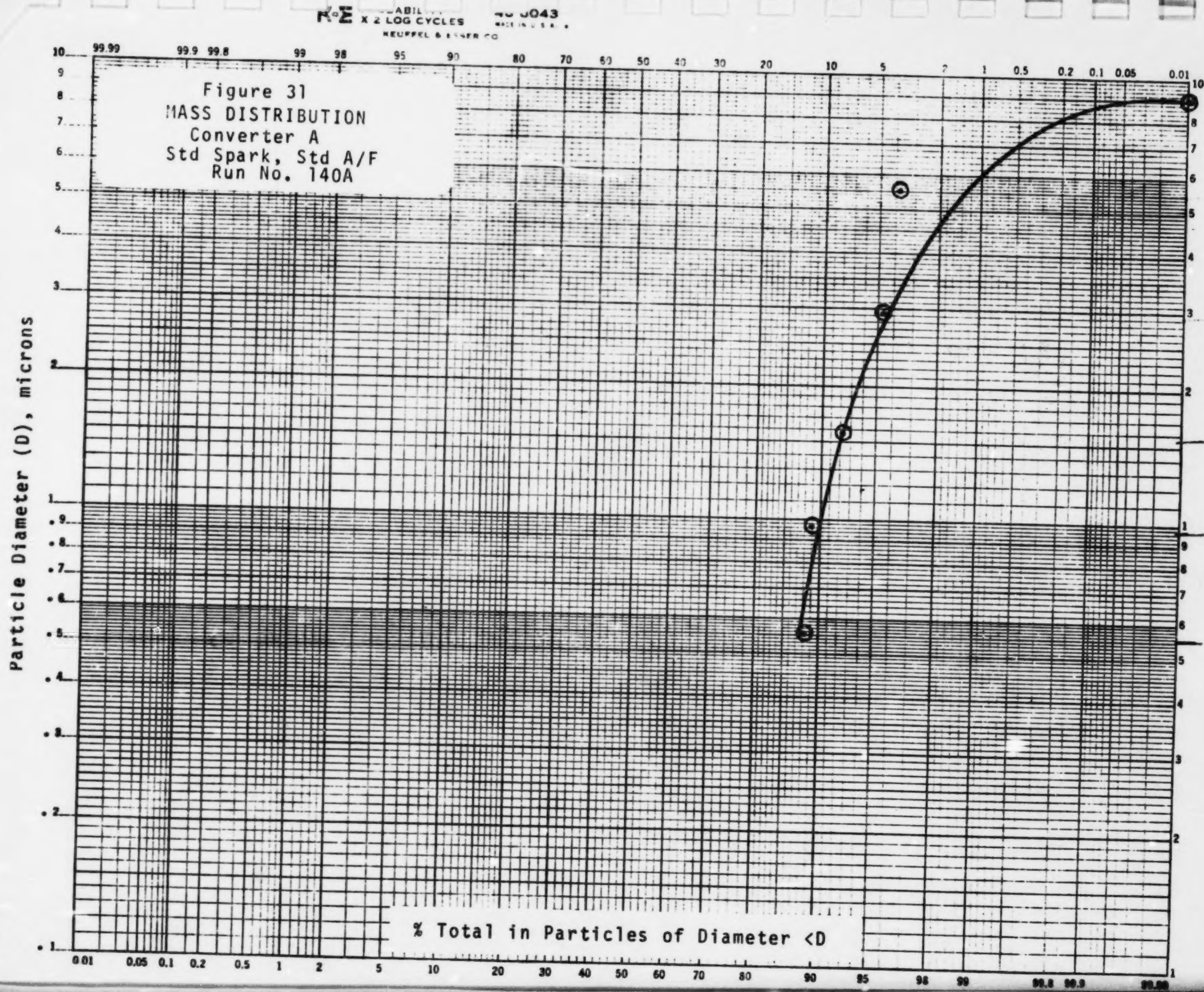


Figure 31
MASS DISTRIBUTION
Converter A
Std Spark, Std A/F
Run No. 140A

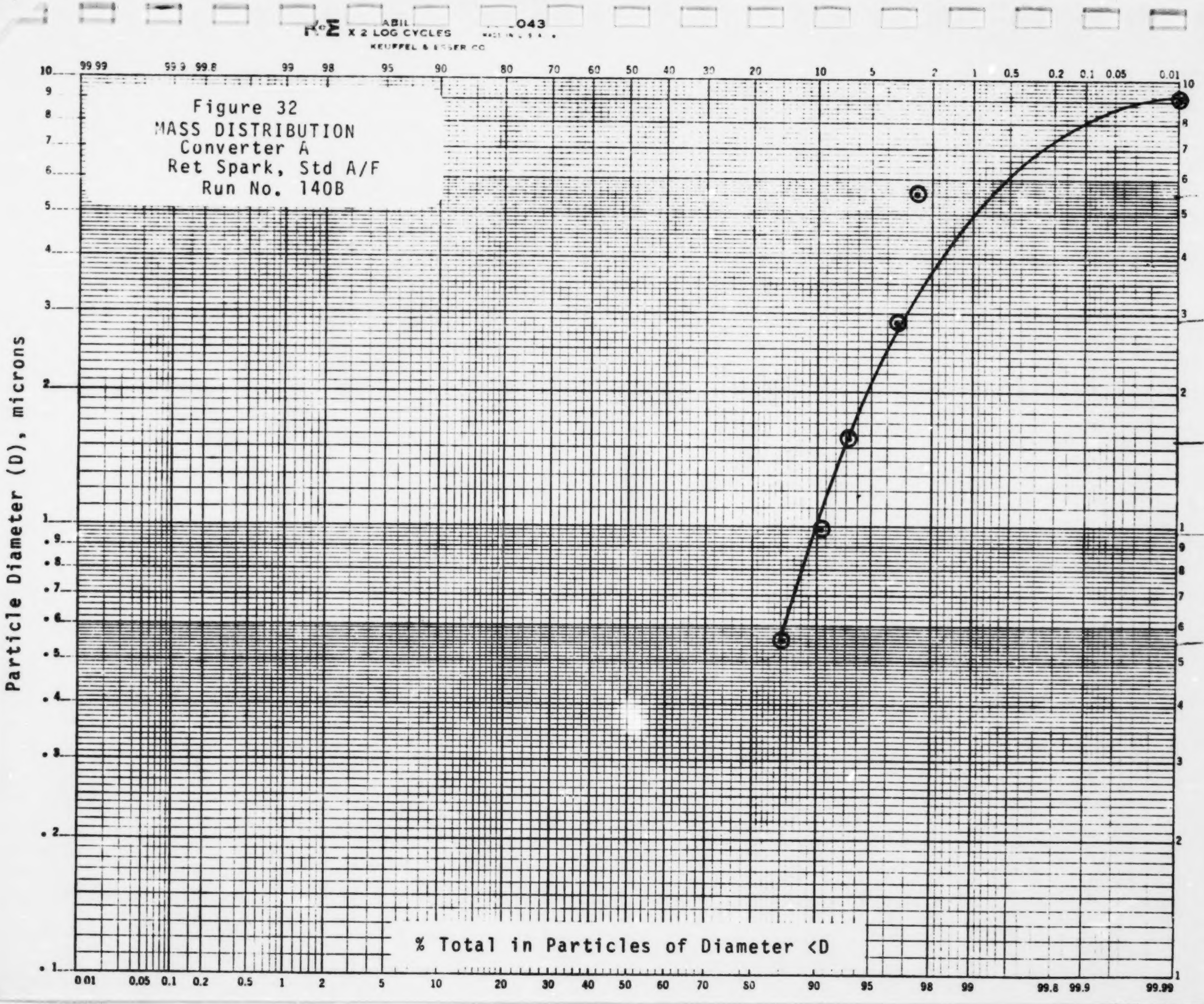


Figure 32
MASS DISTRIBUTION
Converter A
Ret Spark, Std A/F
Run No. 140B

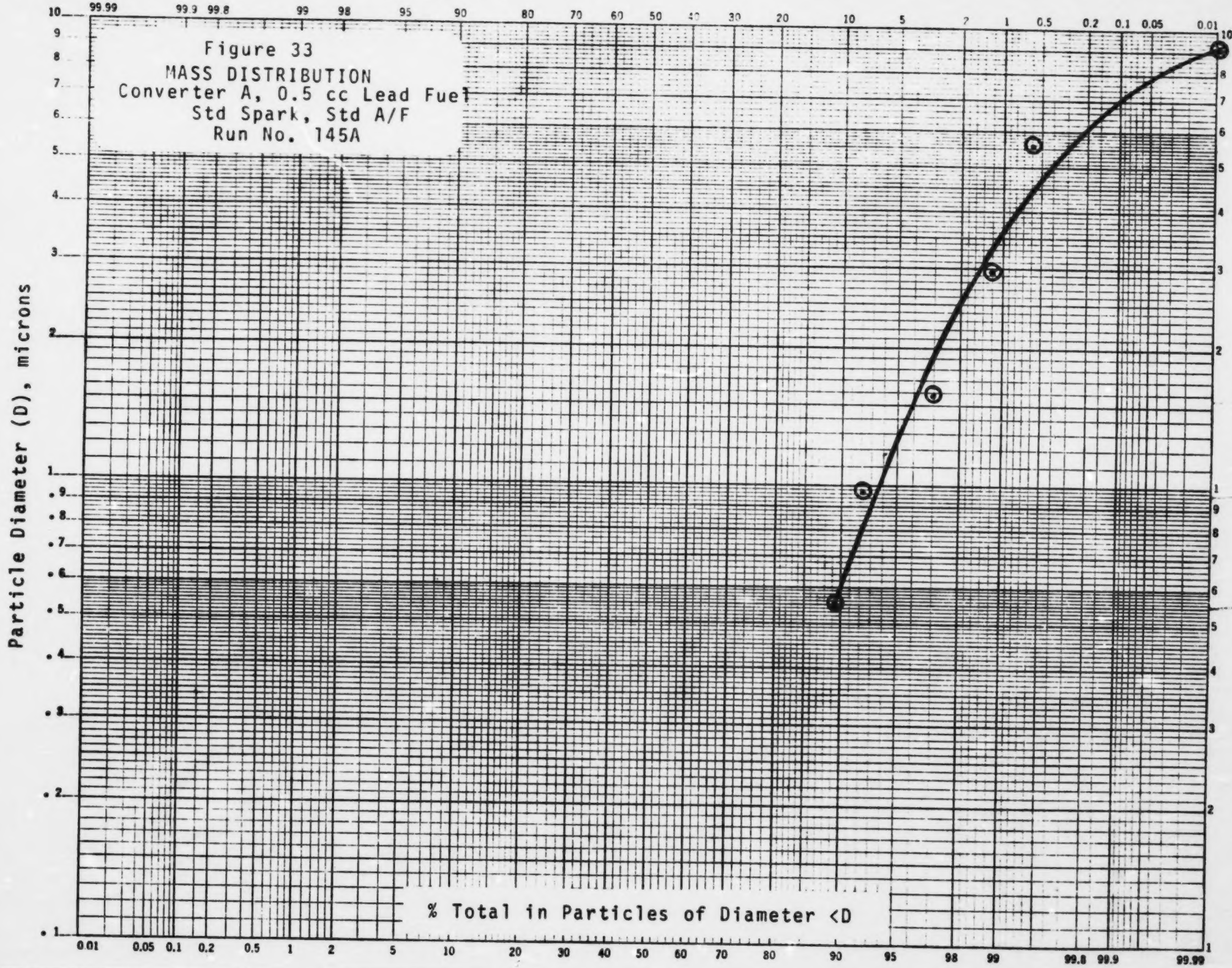


Figure 33
MASS DISTRIBUTION
Converter A, 0.5 cc Lead Fuel
Std Spark, Std A/F
Run No. 145A

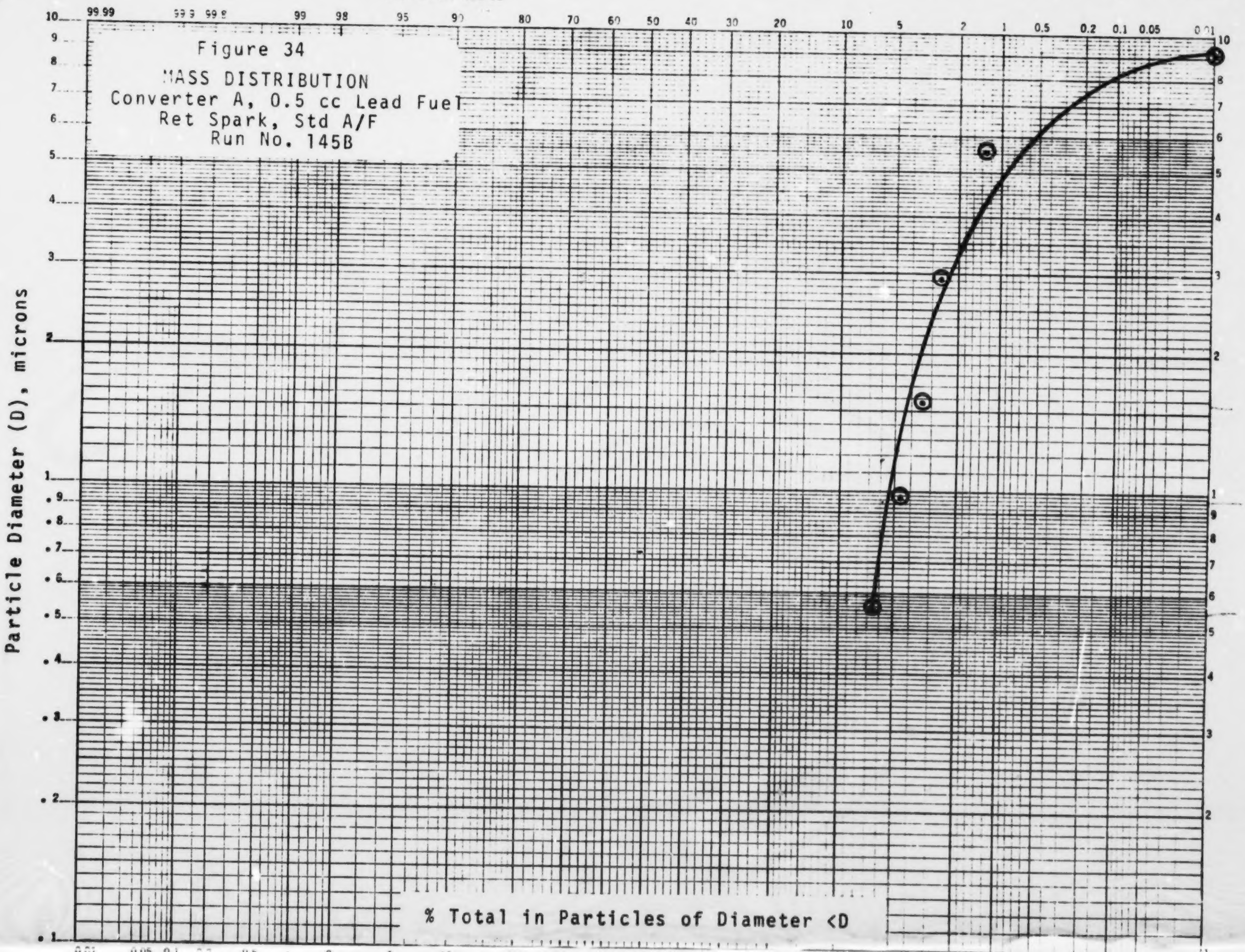


Figure 34

MASS DISTRIBUTION
Converter A, 0.5 cc Lead Fuel
Ret Spark, Std A/F
Run No. 145B

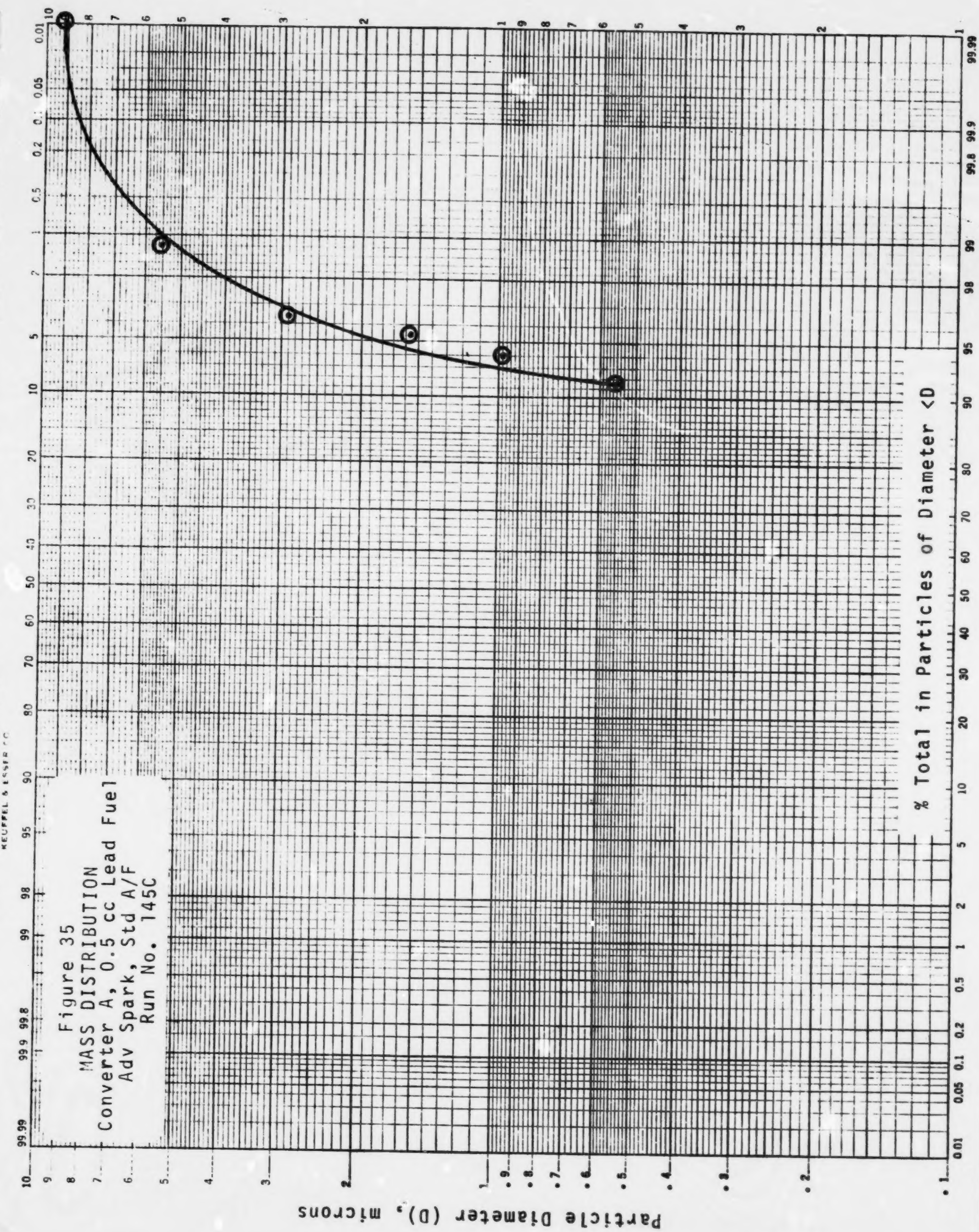


Figure 35
MASS DISTRIBUTION
Converter A, 0.5 cc Lead Fuel
Adv Spark, Std A/F
Run No. 145C

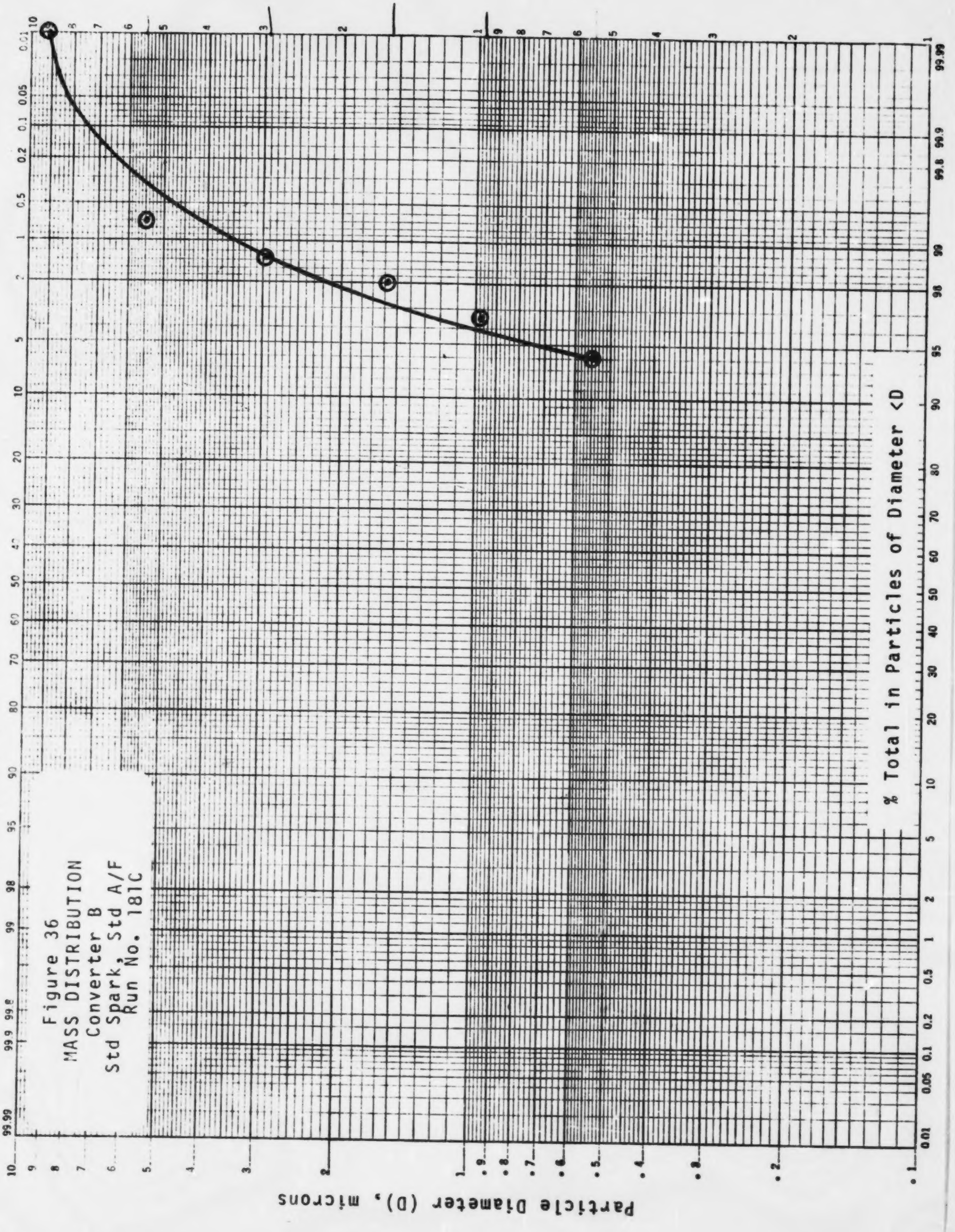


Figure 36
MASS DISTRIBUTION
Converter B
Std Spark, Std A/F
Run No. 181C

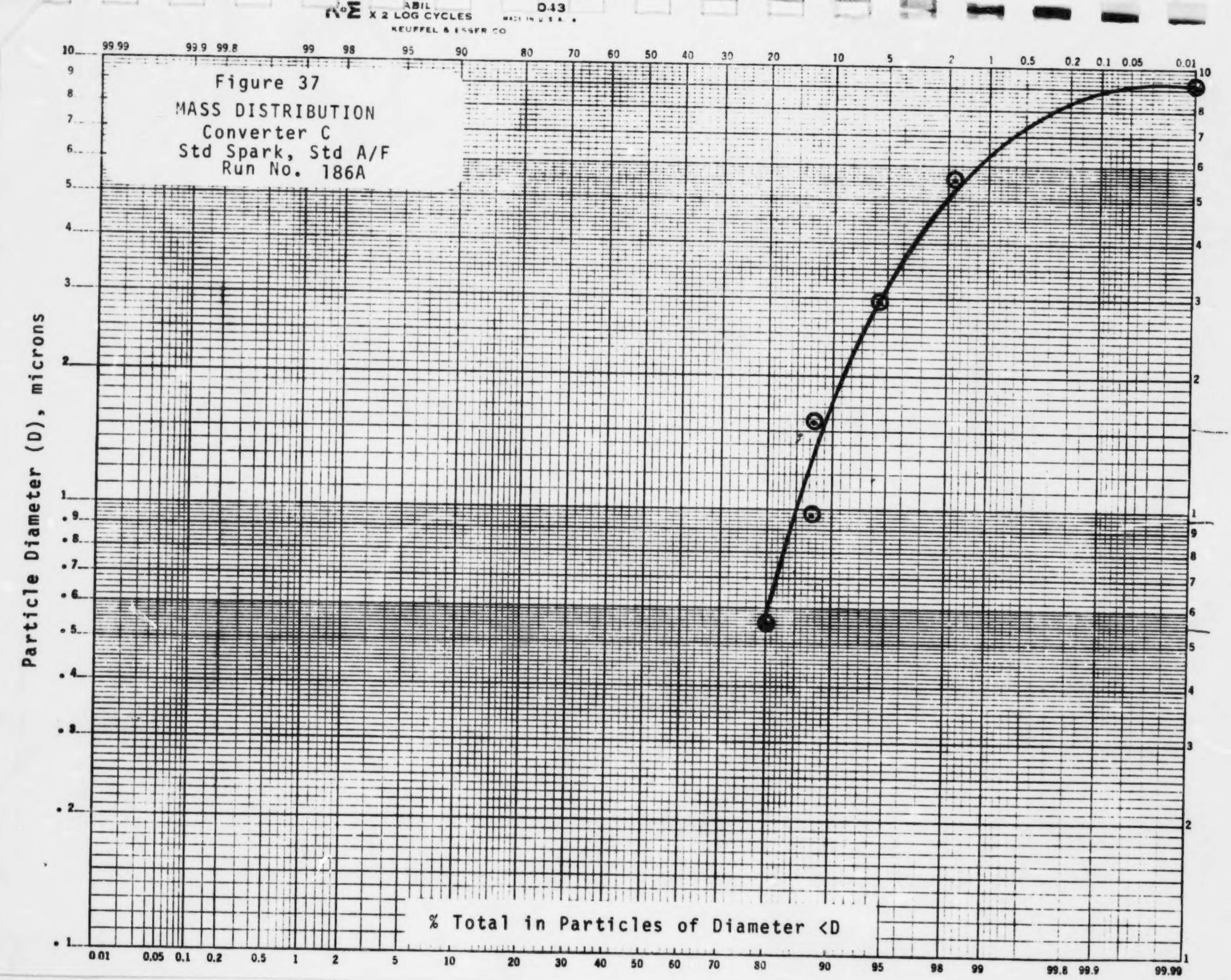


Figure 37

MASS DISTRIBUTION
Converter C
Std Spark, Std A/F
Run No. 186A

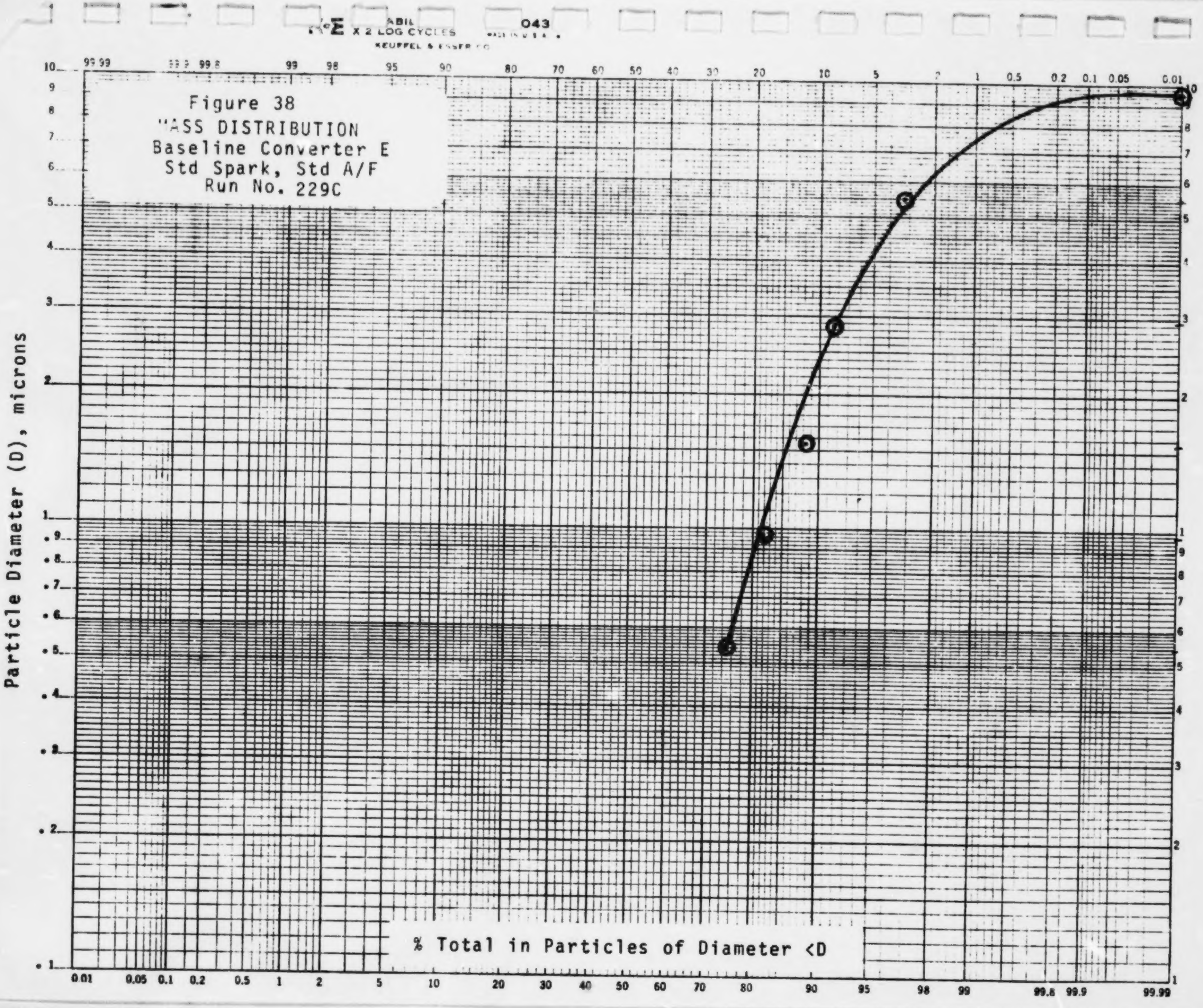


Figure 38
"ASS DISTRIBUTION
Baseline Converter E
Std Spark, Std A/F
Run No. 229C

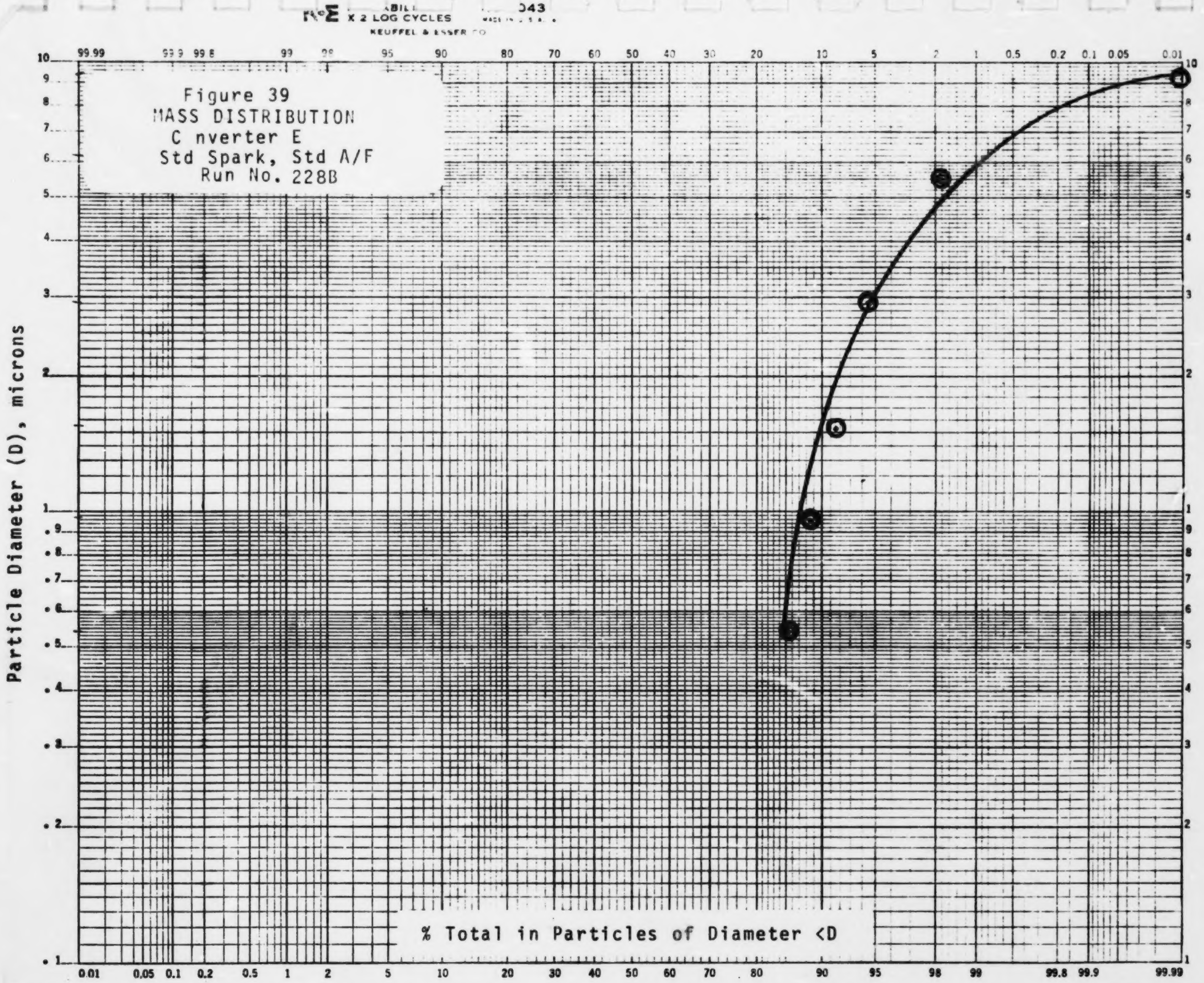


Figure 39
MASS DISTRIBUTION
Converter E
Std Spark, Std A/F
Run No. 228B

The data for Converter D, a reduction catalyst (Table 29), was not plotted or included in the discussions about the other converters, since the conditions under which this converter could be run were so limited. Several runs were aborted because the air/fuel ratios were not in a range which would allow any reduction in NO_x. The runs reported show only a minor reduction in NO_x, but a noticeable increase in particulate mass. This increase was attributed in part to the rich air/fuel ratio necessary for operation of the converter. This device was not run in conjunction with an oxidation catalyst.

A significant decrease in the MMED of the particulate mass collected was noted in the case of all three oxidation catalysts and EGR. The mass size distributions for various runs are plotted in Figure 31-39. Table 32 is a comparison of the distribution to the baseline runs made in Task II (Figures 22-27). As is shown, the percent of the particulate less than 0.55 microns and 0.97 microns increased substantially with the addition of a catalytic device. There was also a significant increase with the addition of 0.5 cc lead. It is interesting to note that Converter A plus leaded fuel was higher than 0.5 lead fuel alone.

The decrease in the particulate size noted when comparing the Converter E baseline to the original baseline is partially explained by the fact that the intake system and carburetor of the engine was modified to take the EGR (Converter E). Thus, the two baselines are not directly comparable. The addition of EGR to the system further decreased the overall particulate size.

TABLE 32

MASS MEDIUM EQUIVALENT DIAMETER FOR BASELINE AND CONVERTERS A, B, C, E

Conditions: 60 mph
Standard Spark
Standard Air/Fuel Ratio

	Baseline		Converter					
	No Lead	0.5 cc Lead	A	A w/0.5 cc Lead	B	C	E	E Baseline
% Particle <0.55 Micron	45	73	88	89	94	80	85	73
% Particle <0.97 Micron	60	87	89	92	97	88	88	82

D. TASK IV

1. Introduction

The objective in Task IV was to evaluate the particulate emission levels of various vehicles equipped with various control devices. Table 33 is a description of the vehicles tested and the number of runs on each one.

2. Conclusions

a. The vehicles on which mileage accumulation tests were made exhibited a large degree of fluctuation with respect to grams/mile of particulate mass as a function of mileage. No clear trends have been established.

b. The precision of measuring particulate mass from a vehicle exhaust was substantially lower than that of measuring an engine stand run, due to the variations in driving conditions prior to testing.

c. In general, the particulate matter which exhibited higher percentages of carbon also exhibited higher parts per million of benzo-α-pyrene.

d. The mass medium equivalent diameter became larger with mileage for two of the three mileage accumulation cars, while decreasing for the other.

e. The mass medium equivalent diameter for the device equipped vehicles in general correlates well with the numbers obtained during the engine stand runs even though the overall mass of the particulate changed.

3. Discussion

The raw data for the vehicles described in Table 33 are presented in Tables 34-43. The mass distribution plots corresponding to

TABLE 33

VEHICLES TESTED AND NUMBER OF RUNS

Vehicle	Series of Runs	Control Device	Vehicle ID	Controlled Emissions
1970 Chevrolet 350 CID	1	Base metal, beaded	ES 60311	HC, CO
1971 Chevrolet 350 CID	3	Noble metal, monolith	61314	HC, CO
1971 Chevrolet 350 CID	3	Base metal, beaded, EGR	61329	HC, CO, NO_x
1972 Pontiac 400 CID	4	Base metal, beaded	2477	HC, CO
1972 Mercedes Benz Diesel	2	None	EPA supplied	-
1971 Oldsmobile 350 CID	1	Not known	EPA supplied	-
1972 Chevrolet 400 CID	2	Particulate trap	PPG	Particulate
Mail Jeep, Ford	1	Stratified charge	EPA 801692	HC, CO, NO_x
1971 Pontiac	1	Questor converter	EPA supplied	HC, CO, NO_x
1970 Chevrolet	1	Thermal reactor, EGR, cyclone collector	Dupont	HC, CO, NO_x, Particulate

the 60 mph steady-state runs in Tables 34-43 are presented in Figures 40-57, and follow the appropriate table. Data for the vehicles as a function of mileage is plotted in Figures 58-62.

Many possible conclusions can be drawn from the large volume of data generated on the various vehicles tested. Several which are thought to be significant will be discussed.

First, it does not appear that any of the mileage accumulation vehicles showed any marked trend toward higher particulate mass levels with time. Car number 61329, a 1972 Chevrolet, increased particulate mass somewhat as measured during a federal cycle hot start, but showed sporadic mass collection rates at the 60 mph steady-state run. Two other cars, the 400 CID Pontiac #2477 and another 1972 Chevrolet #61314, actually decreased slightly with time. This data is plotted in Figures 58-62.

The Pontiac #2477 showed an actual decrease in particulate mass collected when the control device was installed (Figures 60 and 61). This observation was in contrast to the reported increase in particulate mass when oxidation catalysts were installed on an engine stand. An explanation of part of the effect might be that the exhaust system of the vehicle acts as a particle trap in the early stages. However, the 60 mph steady-state results for the Pontiac #2477 showed a general reduction in particulate mass with mileage, out to about 12,000 miles, and the particulate mass collected on the 4 cfm filter stayed essentially constant after installation of the catalyst.

The effect of mileage accumulation on the mass medium equivalent diameter was somewhat inconclusive, since two of the vehicles (Car 61314 and the Pontiac) exhibited increased particulate size with mileage, while the other (Car 61329) showed a particulate size decrease.

TABLE 34

CHASSIS DYNAMOMETER TEST OF CONVERTER EQUIPPED VEHICLES

Car Number: ES 60311
Vehicle Type: 1970 Chevrolet 350 CID
Converter Type: Non-noble Metal - Pelleted

Run No.	Car Miles	Converter Miles	Test Mode	Grams/Mile Particulate				
				Andersen Sampler	Millipore Filter	Andersen + Millipore	Glass Filter	
							1 cfm	4 cfm
68A	80,000	50,000	FC CS	-	-	-	-	.0242
68B	80,000	50,000	FC HS	-	-	-	-	.0016
68C	80,000	50,000	60 mph	-	-	-	-	.0174

Continuation of Table 34

EXHAUST GAS ANALYSIS

Run No.	% by Volume				Parts per Million				Exhaust Condensate (ppm)	
	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x	HCHO	NH_3
68A	-	-	-	-	-	-	-	-	-	-
68B	-	-	-	-	-	-	-	-	-	-
68C	12.6	3.9	82.4	.17	45	32	1450	-	-	-

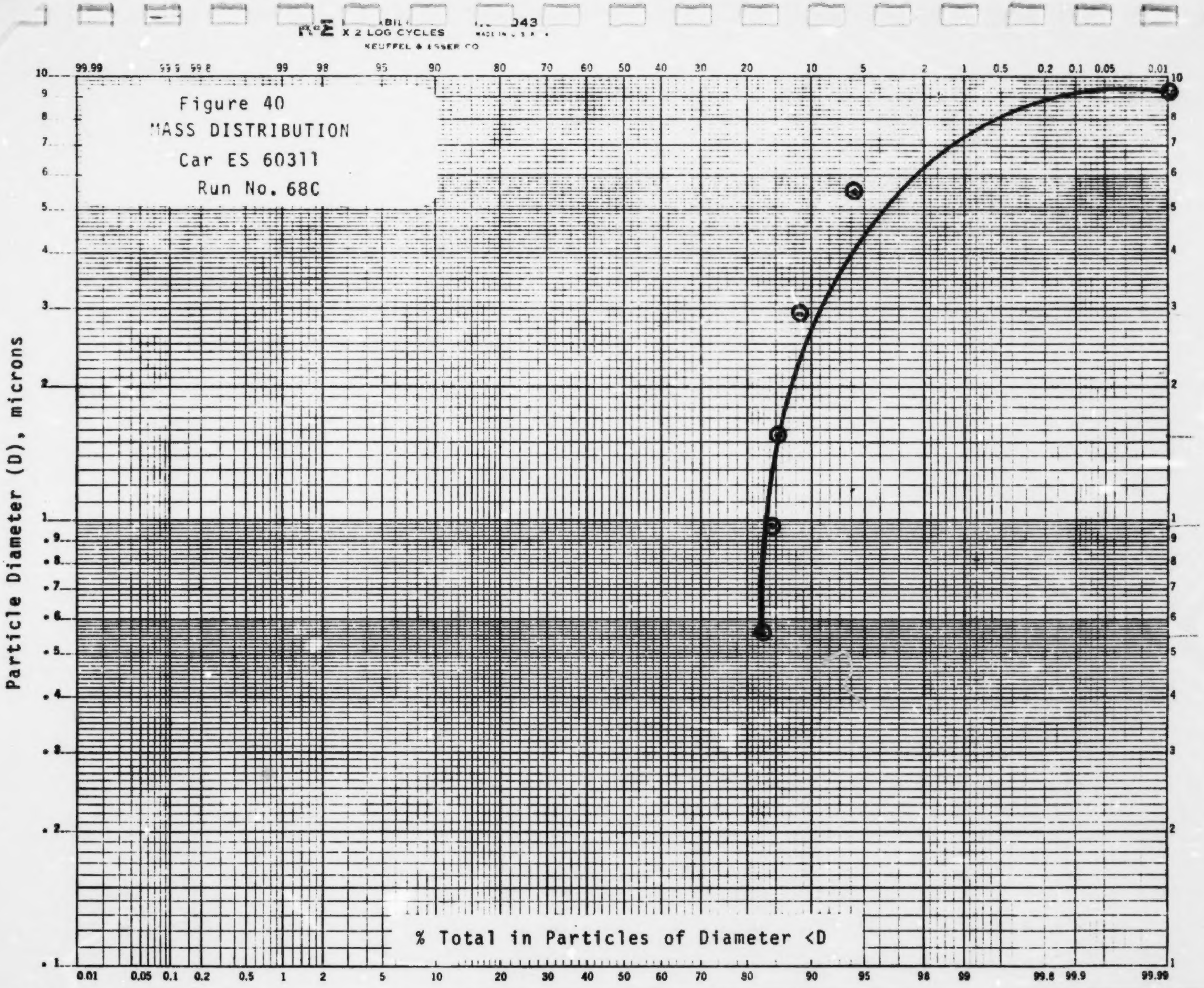


Figure 40
MASS DISTRIBUTION
Car ES 60311
Run No. 68C

TABLE 35
CHASSIS DYNAMOMETER TEST OF CONVERTER EQUIPPED VEHICLES

Car Number: 61314
Vehicle Type: 1971 Chevrolet 350 CID
Converter Type: Noble Metal - Monolithic

Run No.	Car Miles	Converter Miles	Test Mode	Grams/Mile Particulate				
				Andersen Sampler	Millipore Filter	Andersen + Millipore	Glass Filter	
							1 cfm	4 cfm
69A	4,816	-	FC CS	-	-	-	-	.0258
69B	"	-	FC HS	-	-	-	-	.0258
69C	"	-	60 mph	.0035	.0605	.0640	-	.0544
94A	18,299	-	FC CS	-	-	-	-	.0725
94B	"	-	FC HS	-	-	-	-	.0517
189A	34,000	-	FC Mod.	.0456	.0045	.0501	.0159	.0108
189B	"	-	60 mph	.0041	.0010	.0051	.0066	.0058
189C	"	-	FC HS	-	-	-	.0268	.0128
189D	"	-	FC HS	-	-	-	.0525	.0191

Continuation of Table 35

EXHAUST GAS ANALYSIS

Run No.	% by Volume CO_2	% by Volume O_2	% by Volume N_2	% by Volume CO	Parts per Million Total H.C.	Parts per Million NO_2	Parts per Million NO	Parts per Million NO_x	Exhaust Condensate (ppm) HCHO	Exhaust Condensate (ppm) NH_3	ppm in Exhaust Gas HCHO	ppm in Exhaust Gas NH_3
69A	-	-	-	-	-	-	-	-	-	-	-	-
69B	-	-	-	-	-	-	-	-	-	-	-	-
69C	11.2	5.0	82.3	.03	4	50	1200	-	-	-	-	-
94A	-	-	-	-	-	-	-	-	-	-	-	-
94B	-	-	-	-	-	-	-	-	-	-	-	-
189A	-	-	-	-	-	-	-	-	100	6.6	-	-
189B	13.5	3.4	82.2	.03	10	8	1070		51	3.6	2.77	0.34
189C	-	-	-	-	-	-	-	-	-	-	-	-
189D	-	-	-	-	-	-	-	-	-	-	-	-

Continuation of Table 35

ANALYSIS OF EXHAUST PARTICULATE

Run No.	Trace Metals on Millipore Filter (%) Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	Measured in Particulate % Pb Atomic Absorp	% C on Glass Filter	ppm BaP
69A	-	-	-	-	-	-	-	-	-	-	-	-	-	-
69B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
69C	.011	.008	.006	.002	.040	.008	<.001	<.001	<.001	.003	<.001	-	-	<19
94A	-	-	-	-	-	-	-	-	-	-	-	-	-	-
94B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
189A	6.3	<1.0	8.8	2.3	41.0	8.5	<1.0	<1.0	<1.0	4.4	<1.0	-	61.4	100
189B	2.9	<.34	2.1	0.6	16.0	3.7	<.34	40	.34	1.6	<.34	-	13.2	<15
189C	-	-	-	-	-	-	-	-	-	-	-	-	-	-
189D	-	-	-	-	-	-	-	-	-	-	-	-	-	-

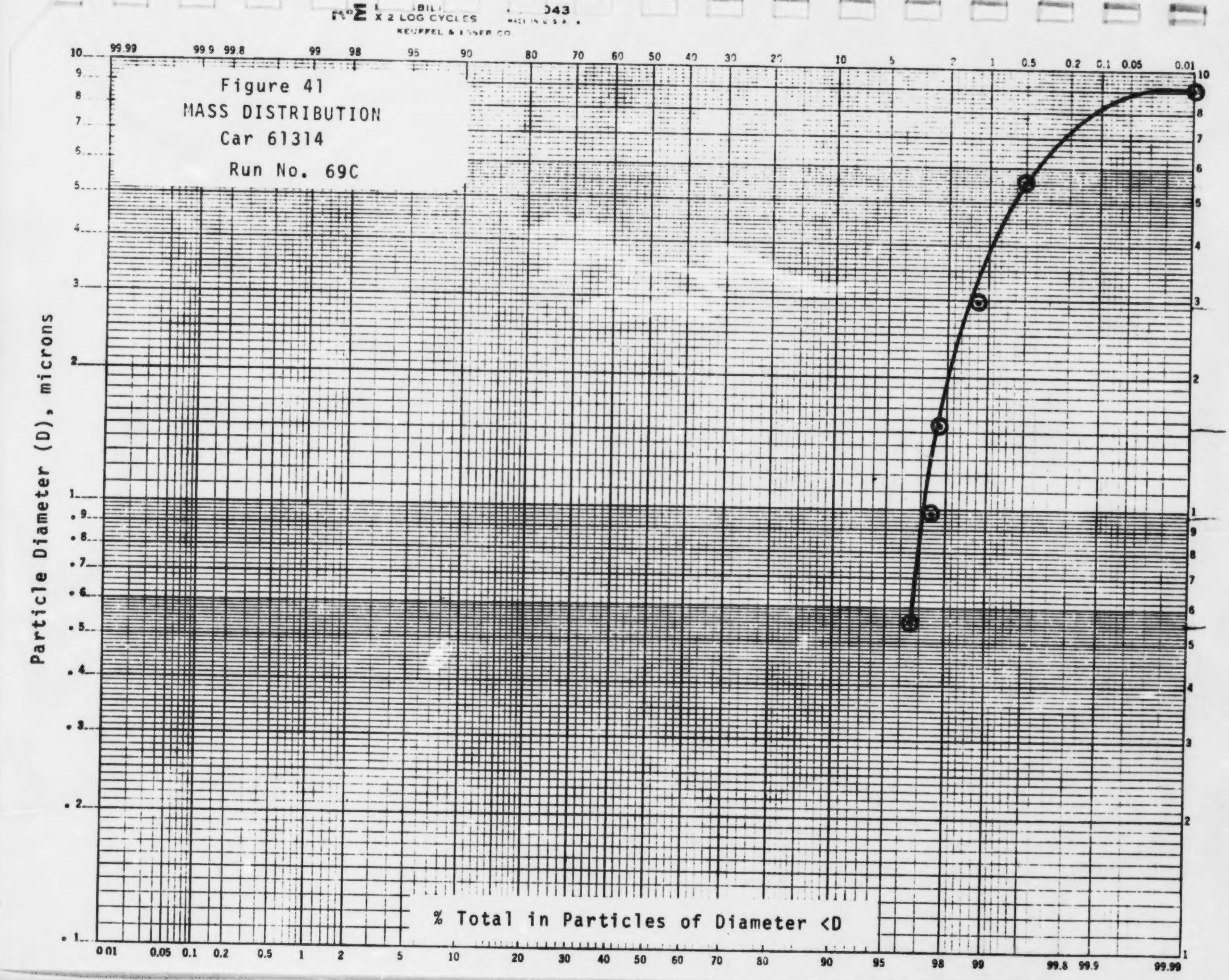


Figure 41
MASS DISTRIBUTION
Car 61314
Run No. 69C

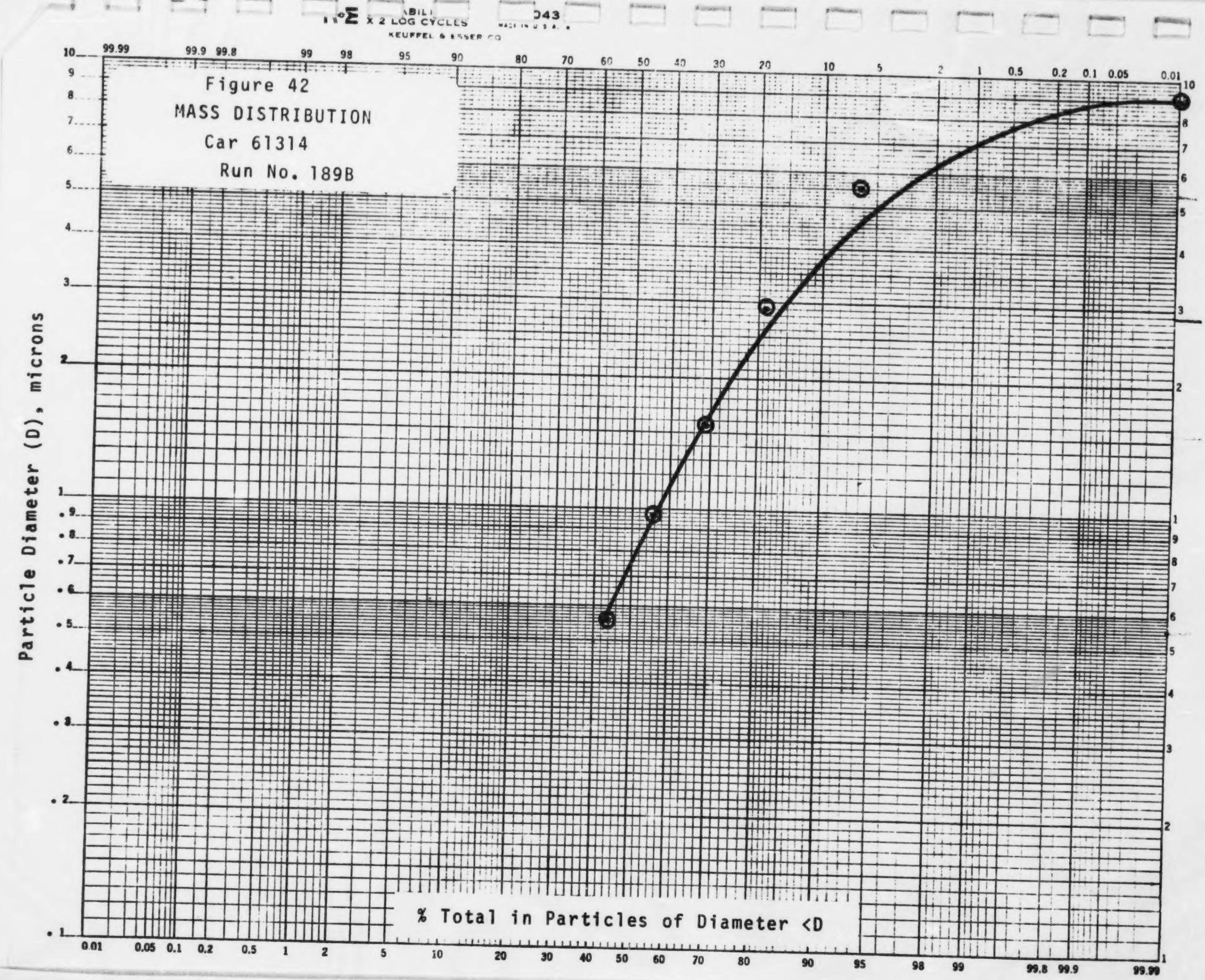


Figure 42
MASS DISTRIBUTION
Car 61314
Run No. 189B

TABLE 36

CHASSIS DYNAMOMETER TEST OF CONVERTER EQUIPPED VEHICLES

Car Number:	61329
Vehicle Type:	1971 Chevrolet 350 CID
Converter Type:	Base Metal Beaded + EGR

Run No.	Car Miles	Converter Miles	Test Mode	Grams/Mile Particulate				
				Andersen Sampler	Millipore Filter	Andersen + Millipore	Glass Filter	
							1 cfm	4 cfm
138A	6,000	2,500	FC HS	-	-	-	.0233	.0070
138B	"	"	FC HS	-	-	-	.0080	.0080
138C	"	"	FC HS	-	-	-	.0149	.0130
139A	6,700	3,200	FC Mod.	.1434	.0130	.1564	.0060	.0087
139B	"	"	60 mph	.0108	.0165	.0273	.0519	.0528
139C	"	"	FC CS	.1533	.0133	.1666	.0166	.0183
204A	11,300	7,800	FC Mod.	.0826	.0087	.0913	.0065	.0054
204B	"	"	60 mph	.0067	.0202	.0269	.0291	.0291
204C	"	"	FC HS	-	-	-	.0200	.0133
204D	"	"	FC HS	-	-	-	.0266	.0147
204E	"	"	FC HS	-	-	-	.0233	.0125
205A	"	"	FC Mod.	.1130	.0174	.1304	.0239	.0097
205B	"	"	60 mph.	.0073	.0368	.0441	.0510	.0487
205C	"	"	FC HS	-	-	-	.0167	.0067
205D	"	"	FC HS	-	-	-	.0100	.0091
205E	"	"	FC HS	-	-	-	.0133	.0108
205F	"	"	FC HS	-	-	-	.0800	.0358
205G	"	"	FC HS	-	-	-	.0733	.0358
205H	"	"	60 mph	.0139	.0032	.0171	.0143	.0073
231A	16,659	13,159	FC Mod.	.0826	.1130	.1956	.0348	.0152
231B	"	"	60 mph	.0068	.0547	.0615	.0620	.0629
231C	"	"	FC Mod.	.0435	.0522	.0957	.0391	.0163
231D	"	"	FC HS	-	-	-	.0300	.0125
231E	"	"	FC HS	-	-	-	.0300	.0142
231D	"	"	FC HS	-	-	-	.0300	.0117

Continuation of Table 36

EXHAUST GAS ANALYSIS

Run	% by Volume				Parts per Million				Exhaust Condensate (ppm)		ppm in Exhaust Gas	
No.	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x	HCHO	NH_3	HCHO	NH_3
138A	-	-	-	-	-	-	-	-	-	-	-	-
138B	-	-	-	-	-	-	-	-	-	-	-	-
138C	-	-	-	-	-	-	-	-	-	-	-	-
139A	-	-	-	-	-	-	-	-	-	-	-	-
139B	11.5	5.8	81.8	.03	10	8	270	-	-	-	-	-
139C	-	-	-	-	-	-	-	-	-	-	-	-
204A	-	-	-	-	-	-	-	-	27.3	-	-	-
204B	11.3	5.8	81.5	.03	5	5	150	-	30.8	16.4	0.92	0.87
204C	-	-	-	-	-	-	-	-	-	-	-	-
204D	-	-	-	-	-	-	-	-	-	-	-	-
204E	-	-	-	-	-	-	-	-	-	-	-	-
205A	-	-	-	-	-	-	-	-	58.5	-	-	-
205B	11.8	5.9	81.3	.03	3	60	1050	-	33.6	2.8	2.0	0.29
205C	-	-	-	-	-	-	-	-	-	-	-	-
205D	-	-	-	-	-	-	-	-	-	-	-	-
205E	-	-	-	-	-	-	-	-	-	-	-	-
205F	-	-	-	-	-	-	-	-	-	-	-	-
205G	-	-	-	-	-	-	-	-	-	-	-	-
205H	11.6	6.37	81.2	.03	28	40	200	-	143.0	13.9	7.8	1.3
231A									50.12	9.73	-	-
231B	12.0	5.4	81.6	.03	5	10	240	-	1.24	2.4	0.07	0.25
231C	-	-	-	-	-	-	-	-	98.9	3.26	-	-
231D	-	-	-	-	-	-	-	-	-	-	-	-
231E	-	-	-	-	-	-	-	-	-	-	-	-
231F	-	-	-	-	-	-	-	-	-	-	-	-

Continuation of Table 36

ANALYSIS OF EXHAUST PARTICULATE

Run No.	Trace Metals on Millipore Filter (%) Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	Measured in Particulate % Pb Atomic Absorp	% C on Glass Filter	ppm BaP
138A	-	-	-	-	-	-	-	-	-	-	-	-	-	-
138B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
138C	-	-	-	-	-	-	-	-	-	-	-	-	-	-
139A	2.3	<.6	2.66	1.0	24	4.0	<.3	<.6	<.6	2.0	<.6	7.5	63.8	320
139B	0.2	<.04	.2	.06	1.6	.26	<.2	<.04	<.01	<.01	<.04	5.0	1.4	<4
139C	3.0	<1.0	6.0	1.5	37	6.0	<.3	<.2	<.6	<.3	<.6	<.1	80.7	<93
204A	1.9	<.5	4.7	<.50	16	1.5	<.5	<.5	<.5	1.6	<.5	Nil	100	670
204B	.056	<.016	.20	<.016	.46	.64	<.01	<.01	.027	.12	<.01	-	<5	<5
204C	-	-	-	-	-	-	-	-	-	-	-	-	-	-
204D	-	-	-	-	-	-	-	-	-	-	-	-	-	-
204E	-	-	-	-	-	-	-	-	-	-	-	-	-	-
205A	-	-	-	-	-	-	-	-	-	-	-	-	-	-
205B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
205C	-	-	-	-	-	-	-	-	-	-	-	-	-	-
205D	-	-	-	-	-	-	-	-	-	-	-	-	-	-
205E	-	-	-	-	-	-	-	-	-	-	-	-	-	-
205F	-	-	-	-	-	-	-	-	-	-	-	-	-	-
205G	-	-	-	-	-	-	-	-	-	-	-	-	-	-
205H	1.2	.20	1.6	.62	9.0	1.8	<.2	.24	<.2	1.2	<.2	<1.3	35.8	<27
231A	8	<2	10	3	64	14	<2	<2	<2	6	4.8	-	-	<120
231B	8	<2	8	3	94	14	<2	<2	<2	10	.2	-	-	57
231C	8	<2	11	4	64	12	<2	<2	<2	8	11.1	-	-	<100
231D	-	-	-	-	-	-	-	-	-	-	-	-	-	-
231E	-	-	-	-	-	-	-	-	-	-	-	-	-	-
231F	-	-	-	-	-	-	-	-	-	-	-	-	-	-

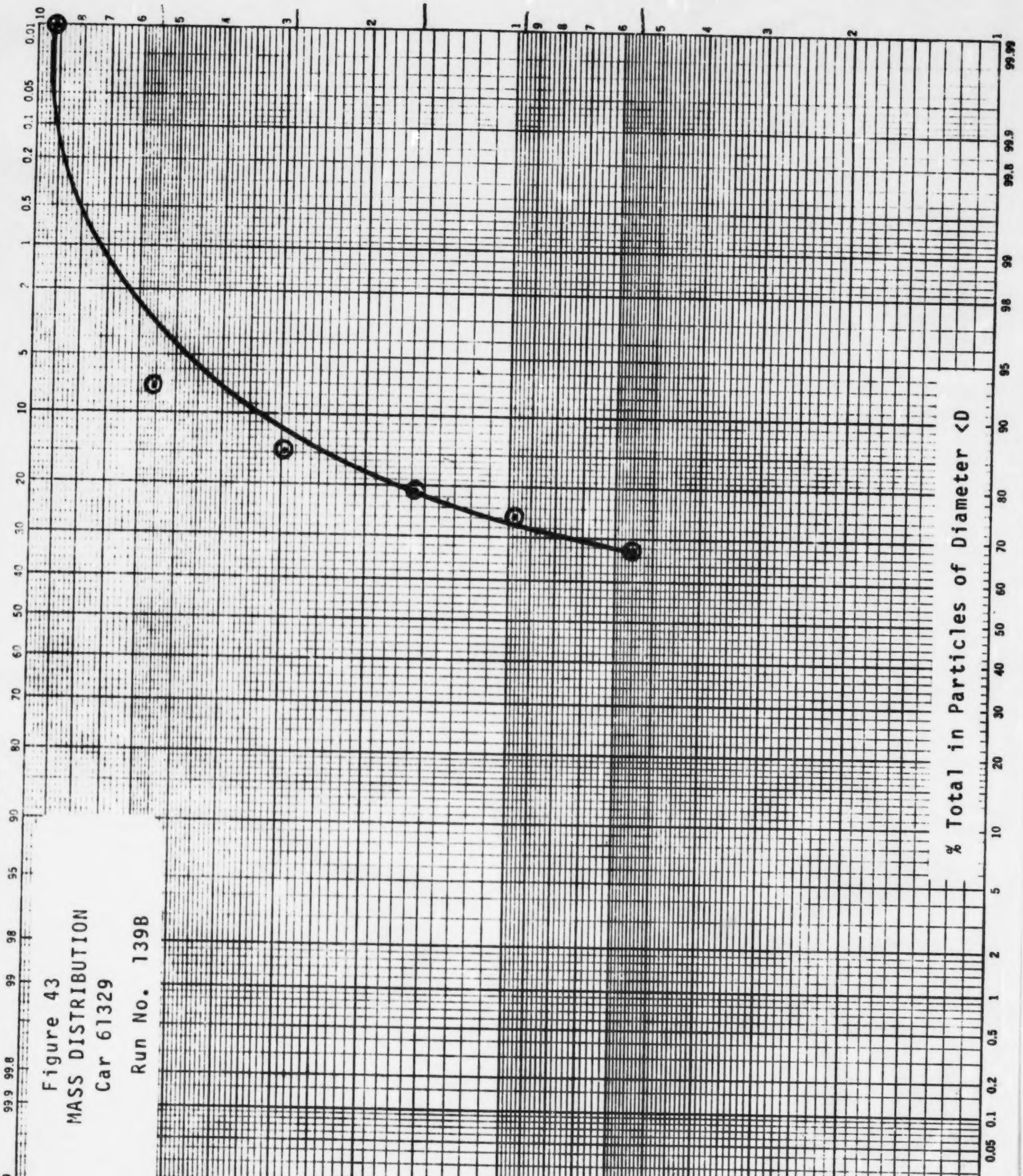


Figure 43
MASS DISTRIBUTION
Car 61329
Run No. 139B

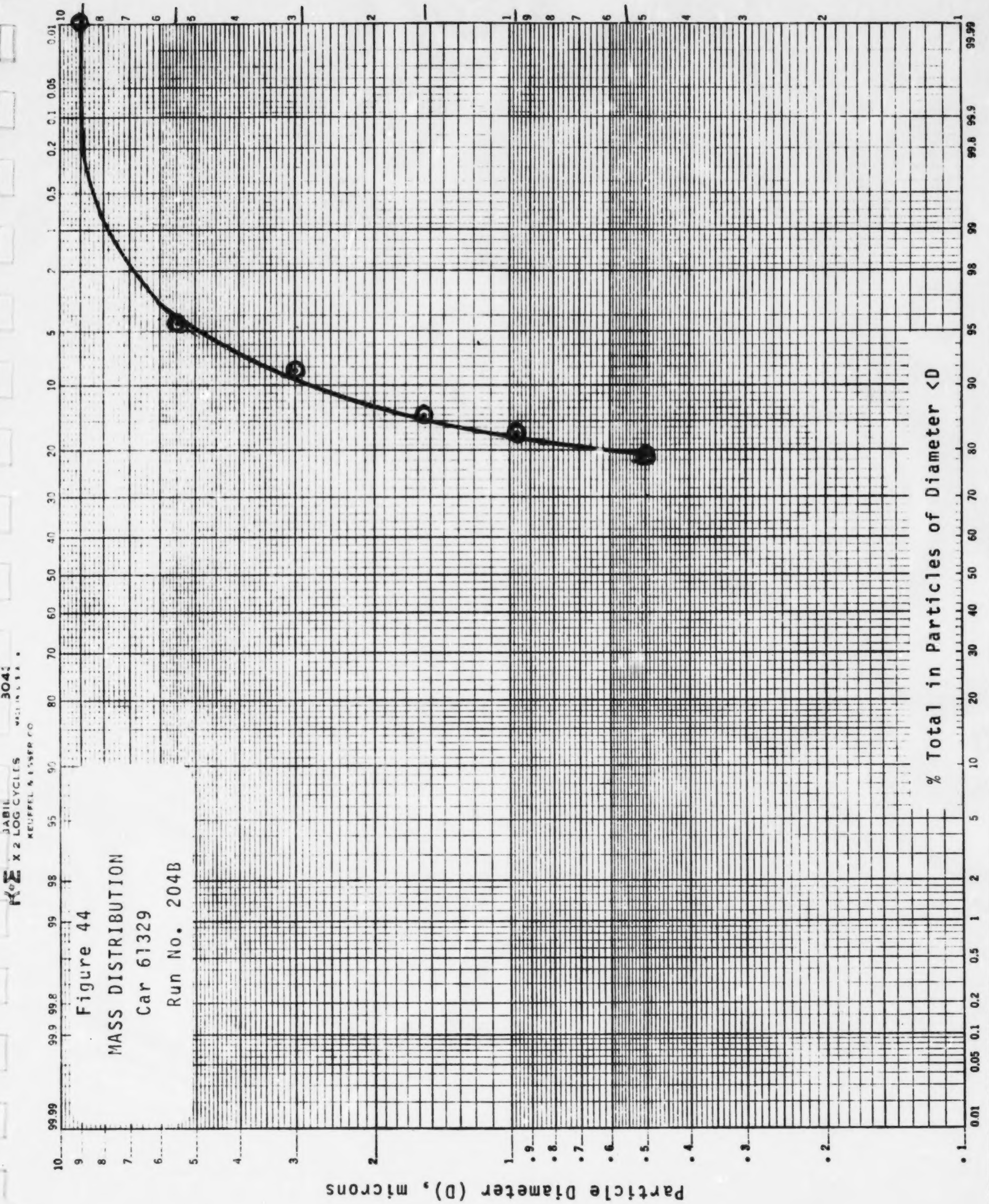


Figure 44
MASS DISTRIBUTION
Car 61329
Run No. 204B

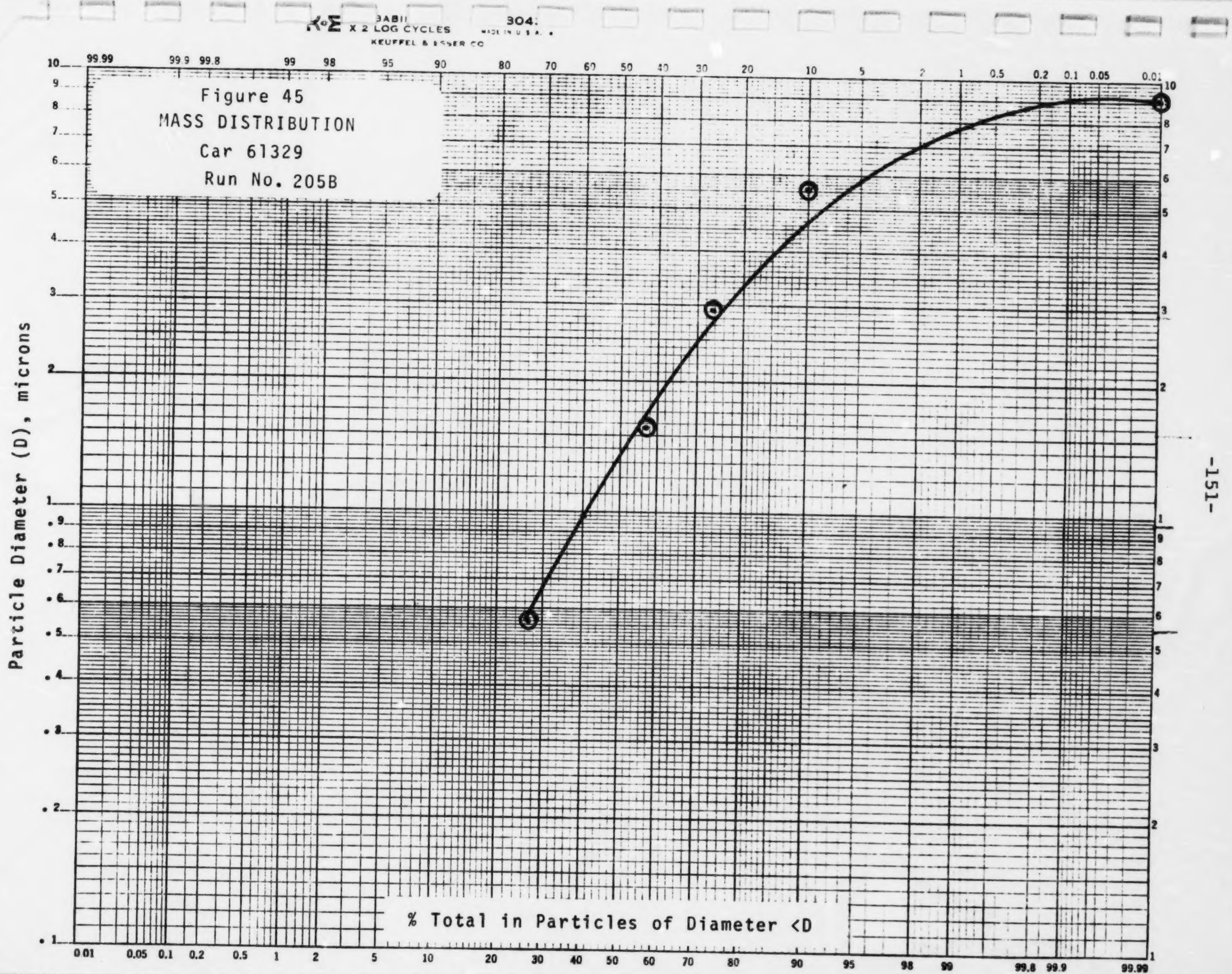


Figure 45
MASS DISTRIBUTION
Car 61329
Run No. 205B

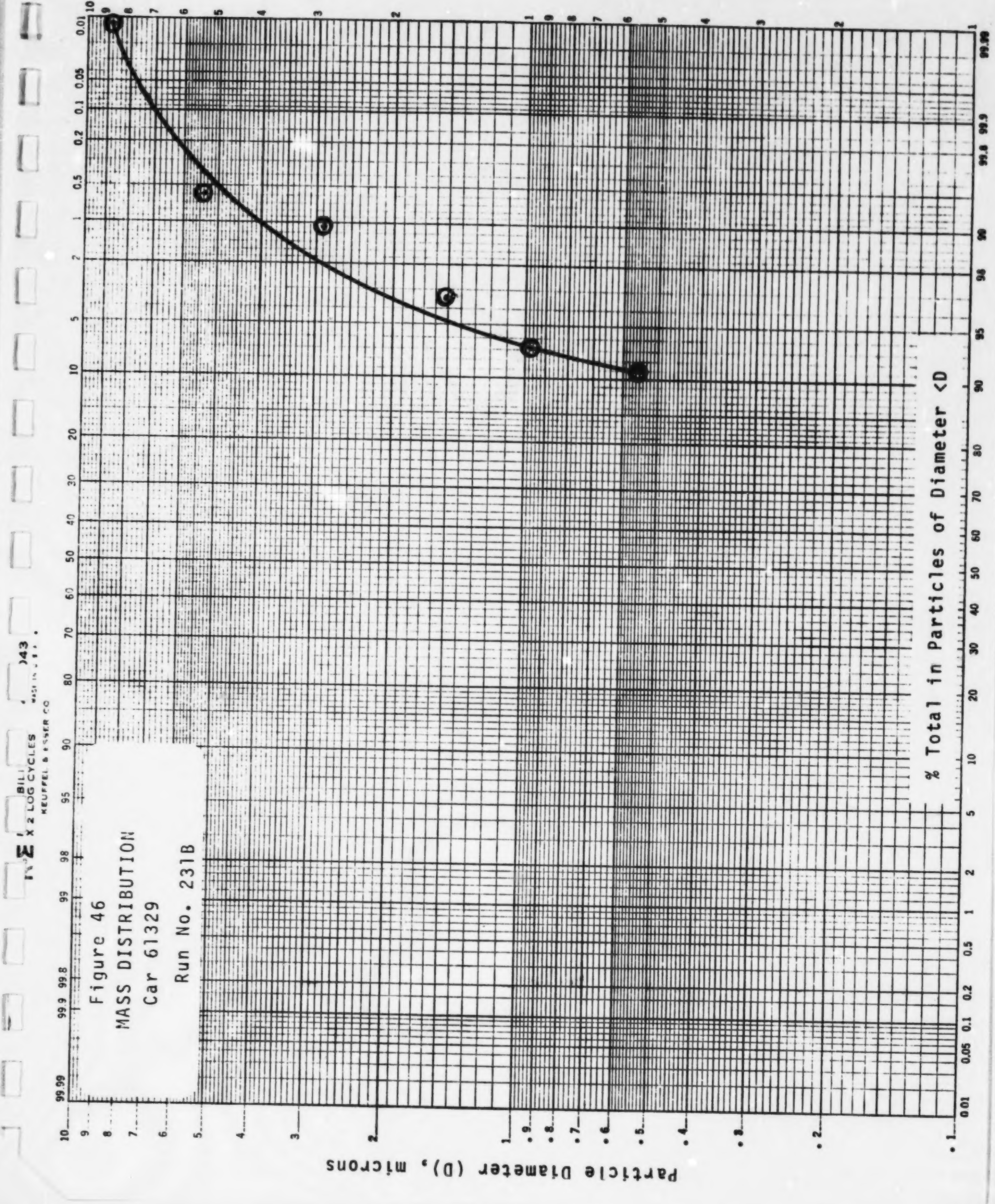


Figure 46
MASS DISTRIBUTION
Car 61329
Run No. 231B

TABLE 37

CHASSIS DYNAMOMETER TEST OF CONVERTER EQUIPPED VEHICLES

Car Number: 2477
Vehicle Type: 1972 Pontiac 400 CID
Converter Type: Base Metal Beaded "C"

Run No.	Car Miles	Converter Miles	Test Mode	Grams/Mile Particulate				
				Andersen Sampler	Millipore Filter	Andersen + Millipore	Glass Filter	
							1 cfm	4 cfm
162A	4,325	455	FC Mod.	.1087	.0826	.1913	.0196	.0163
162B	"	"	60 mph	.0197	.0636	.0833	.0504	.0440
162C	"	"	FC CS	.1267	.1800	.3067	.0200	.0067
162D	"	"	FC HS	-	-	-	.0040	.0040
177A	6,000	2,130	FC Mod.	.0478	.0652	.1130	.2282	.0163
177B	"	"	60 mph	.0053	.0373	.0426	.0360	.0337
177C	"	"	FC CS	.0866	.1266	.2132	.0200	.0100
206A	10,841	6,971	FC Mod.	.0869	.0869	.1738	.0239	.0163
206B	"	"	60 mph	.0071	.0515	.0586	.0385	.0473
206C	"	"	FC HS	-	-	-	.0233	.0133
206D	"	"	FC HS	-	-	-	.0266	.0133
206E	"	"	FC HS	-	-	-	.0333	.0166
206F	"	"	FC CS	.1333	.0133	.1466	.0500	.0200
206G	"	"	FC HS	-	-	-	.0333	.0142
206H	"	"	FC HS	-	-	-	.0300	.0117
226A	15,851	11,981	FC Mod.	.0826	.0651	.1477	.0413	.0174
226B	"	"	60 mph	.0062	.0329	.0391	.0257	.0229
226C	"	"	FC Mod.	.0478	.0130	.0608	.0456	.0163
226D	"	"	FC HS	-	-	-	.0499	.0566
226E	"	"	FC HS	-	-	-	.0466	.0599
			Car before converter or 1975 hardware was installed					
121A	2,000	-	FC Mod.	.1391	.1087	.2478	.0652	.0402

Continuation of Table 37

EXHAUST GAS ANALYSIS

Run No.	% by Volume				Parts per Million				Exhaust Condensate (ppm)		ppm in Exhaust Gas	
	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x	HCHO	NH_3	HCHO	NH_3
162A	-	-	-	-	-	-	-	-	-	-	-	-
162B	11.6	6.5	81.0	.03	2	100	1150	-	-	-	-	-
162C	-	-	-	-	-	-	-	-	-	-	-	-
162D	-	-	-	-	-	-	-	-	-	-	-	-
177A	-	-	-	-	-	-	-	-	7.0	19	-	-
177B	11.9	5.4	81.8	.03	5	40	1100	-	3.2	8	-	-
177C	-	-	-	-	-	-	-	-	20	3	-	-
206A	-	-	-	-	-	-	-	-	177.8	-	-	-
206B	13.0	4.27	81.8	.03	15	8	850	-	11.5	4.41	0.72	0.49
206C	-	-	-	-	-	-	-	-	-	-	-	-
206D	-	-	-	-	-	-	-	-	-	-	-	-
206E	-	-	-	-	-	-	-	-	-	-	-	-
206F	-	-	-	-	-	-	-	-	26.14	-	-	-
206G	-	-	-	-	-	-	-	-	-	-	-	-
206H	-	-	-	-	-	-	-	-	-	-	-	-
226A	-	-	-	-	-	-	-	-	36.38	-	-	-
226B	11.3	6.4	81.4	.03	15	100	1600	-	115.4	-	5.8	-
226C	-	-	-	-	-	-	-	-	77.4	-	-	-
226D	-	-	-	-	-	-	-	-	-	-	-	-
226E	-	-	-	-	-	-	-	-	-	-	-	-
Car before converter or 1975 hardware was installed												
121A	-	-	-	-	-	-	-	-	-	-	-	-

Continuation of Table 37

ANALYSIS OF EXHAUST PARTICULATE

Run No.	Trace Metals on Millipore Filter (%)											Measured in Particulate		
	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	% Pb Atomic Absorp	% C on Glass Filter	ppm BaP
162A	.28	<.05	.43	.28	4.3	.48	<.02	<.05	<.05	<.16	<.05	2.5	23.2	100
162B	.041	<.006	.042	.020	.44	.05	<.003	.024	<.006	<.016	<.006	12.5	1.2	<4
162C	.22	<.037	.24	.28	2.9	.35	<.019	.05	.041	.19	<.031	10.0	.5	<93
162D														
177A	.54	.073	.43	.17	3.1	.71	<.067	<.067	<.067	<.2	<.06	<2.5	-	<83
177B	.087	.016	.046	.013	.35	.08	<.009	.022	<.009	<.03	<.004	5.0	-	<5
177C	.41	<.05	.37	.084	2.0	.48	<.053	<.053	<.053	<.16	<.053	2.5	-	<93
206A	.28	<.05	.23	.085	1.5	.30	<.05	<.05	<.05	<.15	<.05	Nil	13.6	180
206B	.063	<.006	.069	.020	.22	.05	<.006	.016	<.006	<.95	<.006	<.2	1.4	6
206C	-	-	-	-	-	-	-	-	-	-	-	-	-	-
206D	-	-	-	-	-	-	-	-	-	-	-	-	-	-
206E	-	-	-	-	-	-	-	-	-	-	-	-	-	-
206F	-	-	-	-	-	-	-	-	-	-	-	-	-	-
206G	-	-	-	-	-	-	-	-	-	-	-	-	-	-
206H	-	-	-	-	-	-	-	-	-	-	-	-	-	-
226A	10	<2	10	4	78	15	<2.	<2	<2	<6	<2	-	-	130
226B	-	-	-	-	-	-	-	-	-	-	-	-	-	11
226C	8	<2	6	4	66	14	<2	<2	<2	<6	<2	-	-	<43
226D	-	-	-	-	-	-	-	-	-	-	-	-	-	-
226E	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Car before converter or 1975 hardware was installed														-
121A	.32	<.08	.24	.08	2.76	.40	.04	.04	.08	.08	.24	.56	61.2	-

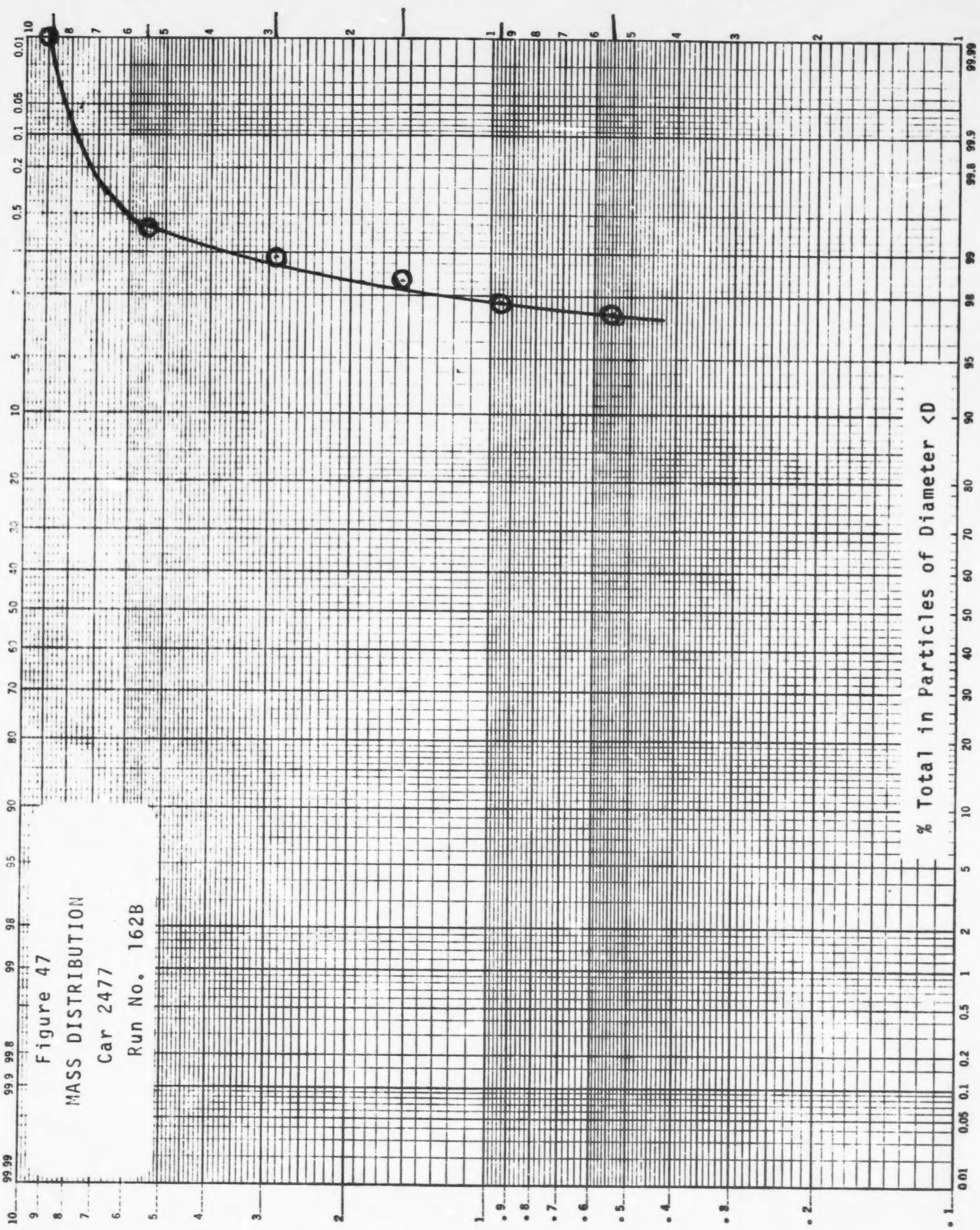
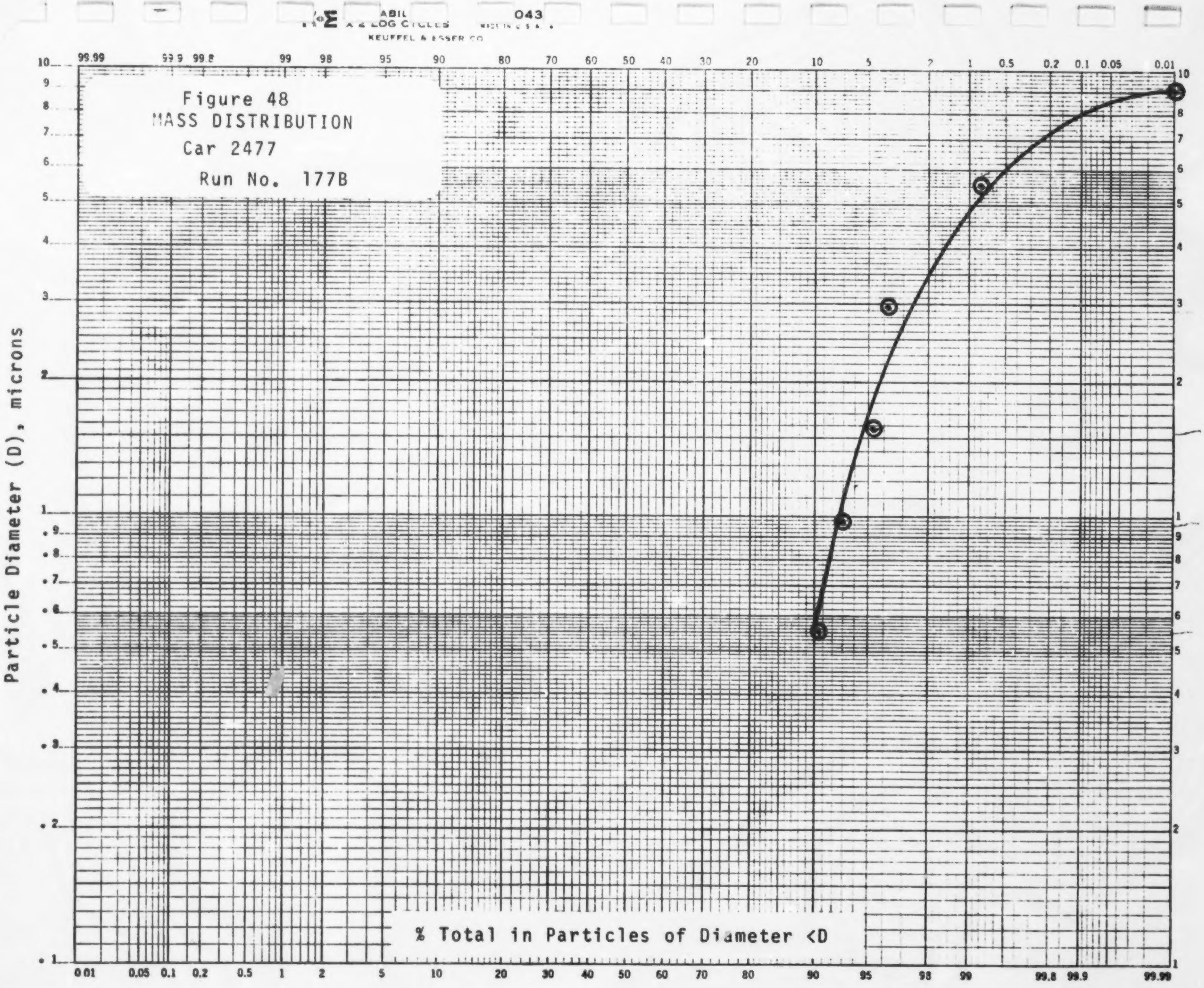


Figure 47
MASS DISTRIBUTION
Car 2477
Run No. 162B

Figure 48
MASS DISTRIBUTION
Car 2477
Run No. 177B



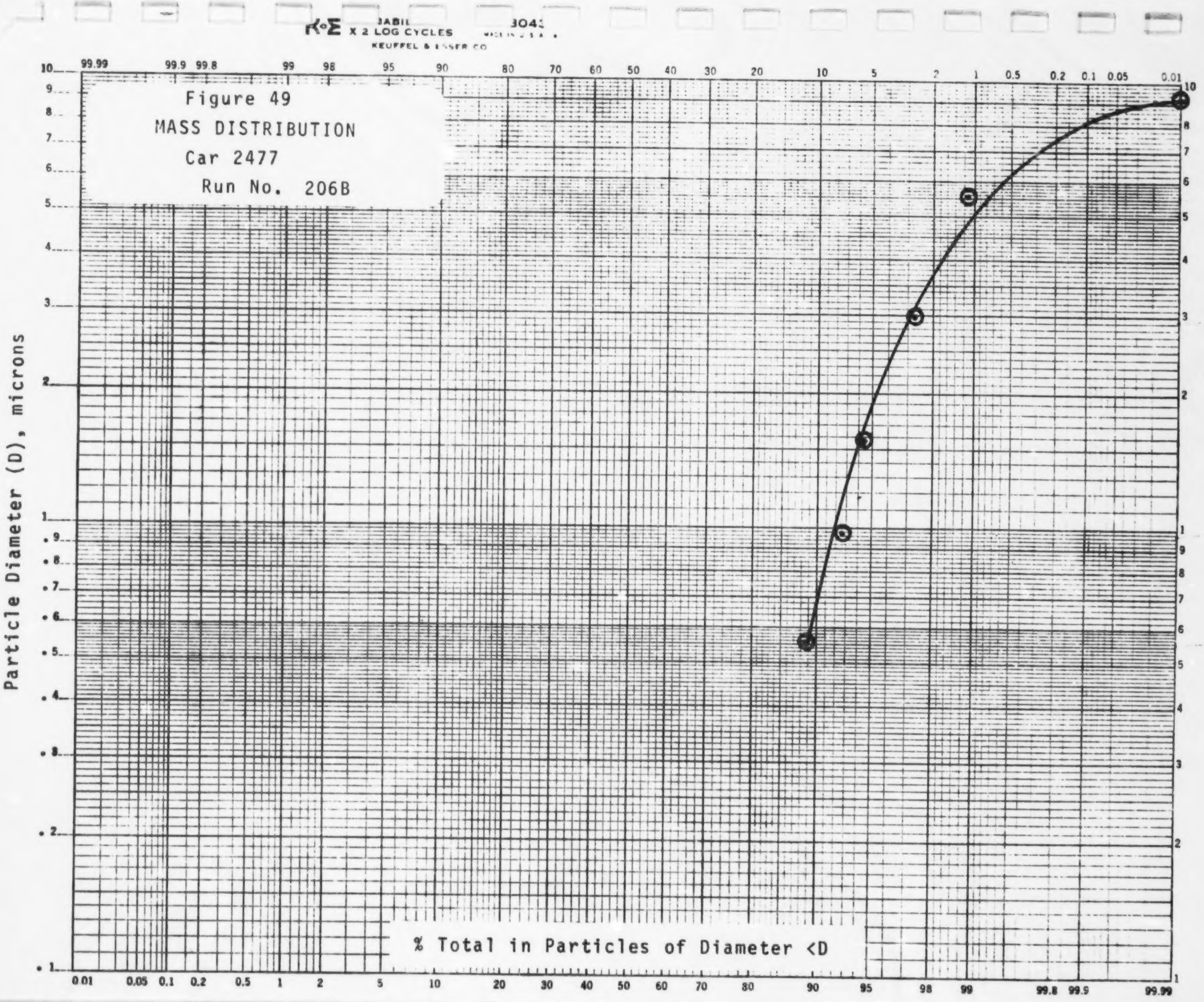


Figure 49
MASS DISTRIBUTION
Car 2477
Run No. 206B

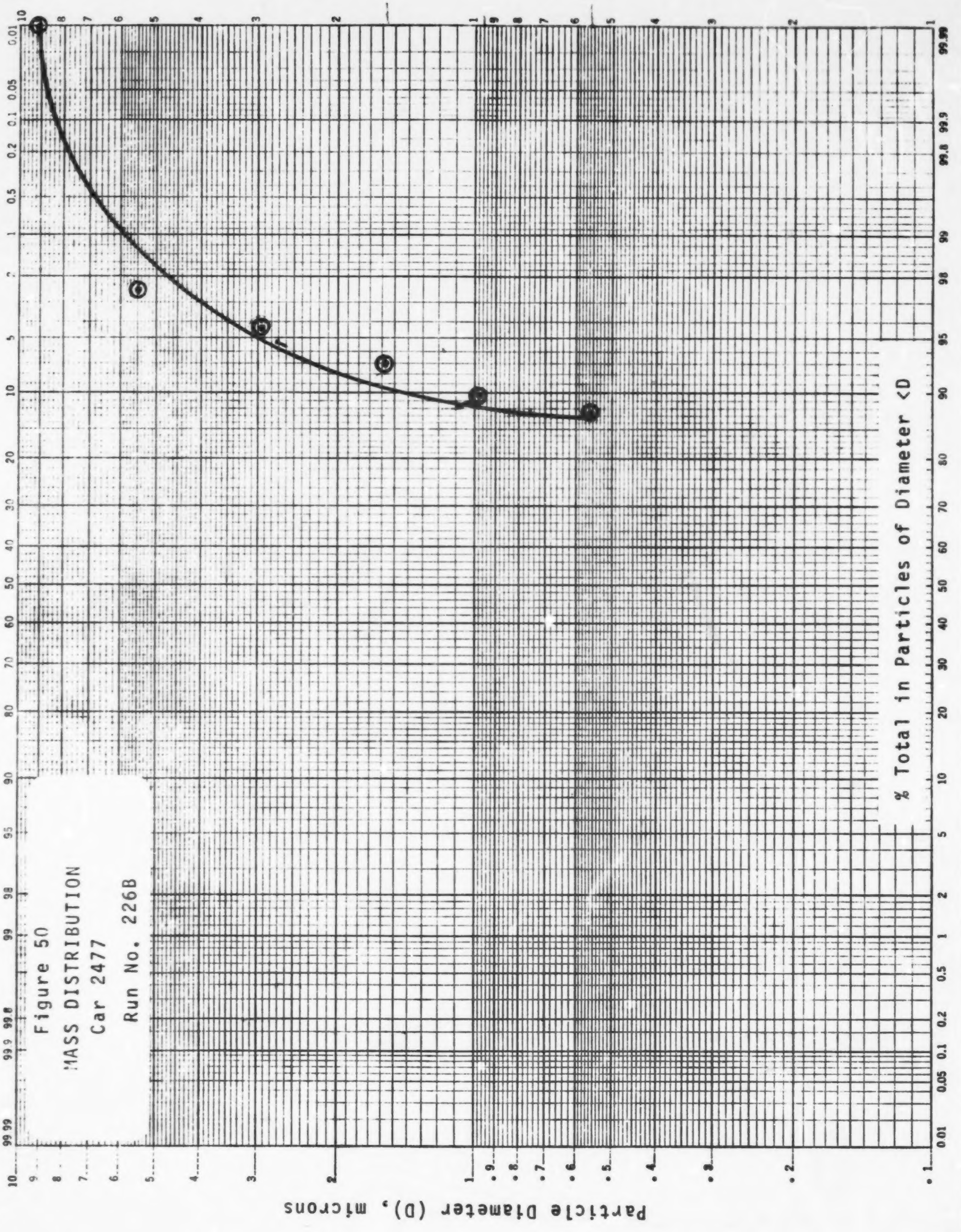


Figure 50
MASS DISTRIBUTION
Car 2477
Run No. 226B

TABLE 38

CHASSIS DYNAMOMETER TEST OF CONVERTER EQUIPPED VEHICLES

Car Number: Environmental Protection Agency
Vehicle Type: 1972 Mercedes Benz Diesel (220)
Converter Type: None

				Grams/Mile Particulate				
Run No.	Car Miles	Converter Miles	Test Mode	Andersen Sampler	Millipore Filter	Andersen + Millipore	Glass Filter	
							1 cfm	4 cfm
163A	3,171	-	FC Mod.	.1735	.4657	.6392	.7715	.6642
217A	6,250	-	FC Mod.	.2739	2.7696	3.0435	.6261	.5371
217B	"	-	FC HS	.2333	2.3333	2.5666	.5833	.4849
217C	"	-	FC HS	.2333	2.3066	2.539	.5633	.4599
217D	"	-	60 mph	.0390	.4784	.5174	.2536	.20217

Continuation of Table 38

EXHAUST GAS ANALYSIS

Run No.	% by Volume CO_2	O_2	N_2	CO	Parts per Million Total H.C.	NO_2	NO	NO_x	Exhaust Condensate (ppm) HCHO	NH_3	ppm in Exhaust Gas HCHO	NH_3
163A									66	-	-	-
217A									71.5	9.2	-	-
217B				No gaseous analyses					50.9	4.24	-	-
217C									-	-	-	-
217D									19.9	5.25	0.78	0.36

Continuation of Table 38

ANALYSIS OF EXHAUST PARTICULATE

Run No.	Trace Metals on Millipore Filter (%)											Measured in Particulate		
	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	% Pb Atomic Absorp	% C on Glass Filter	ppm BaP
163A	.059	.01	.067	.038	.74	.087	.005	.012	.01	.07	.01	.1	80.0	<3
217A	.03	-	.007	.05	-	.02	-	-	-	-	-	.06	75.0	24
217B	.04	-	.003	.03	-	.01	-	-	-	-	-	.05	80.5	5
217C	.007	-	.002	.005	-	.002	-	-	-	-	-	.09	83.3	-
217D	-	-	-	-	-	-	-	-	-	-	-	-	-	4

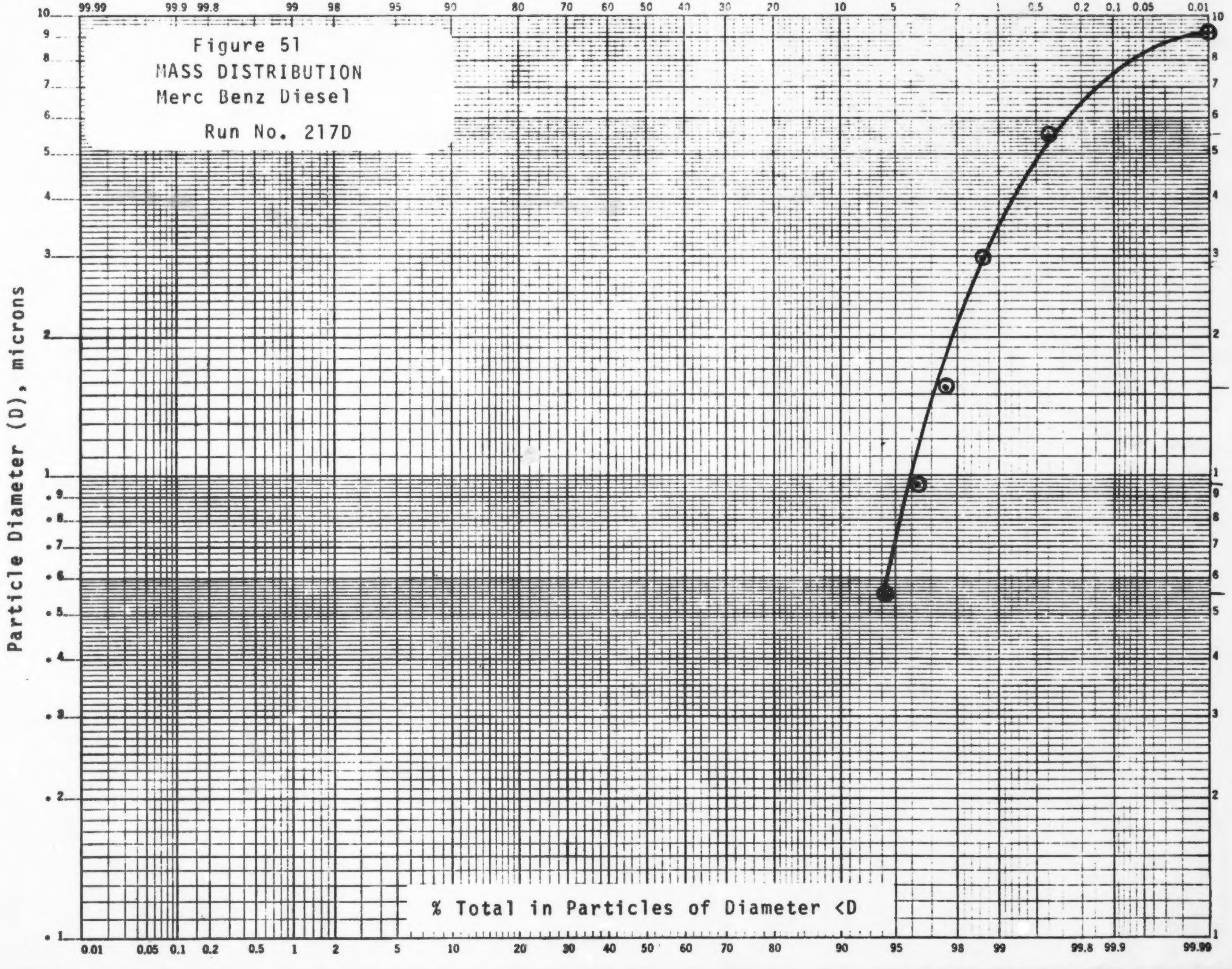


Figure 51
MASS DISTRIBUTION
Merc Benz Diesel
Run No. 217D

TABLE 39

CHASSIS DYNAMOMETER TEST OF CONVERTER EQUIPPED VEHICLES

Car Number: Environmental Protection Agency

Vehicle Type: 1971 Oldsmobile DRX 401 - 350 CID

Converter Type: Not known

Run No.	Car Miles	Converter Miles	Test Mode	Grams/Mile Particulate: Andersen Sampler	Grams/Mile Particulate: Millipore Filter	Grams/Mile Particulate: Andersen + Millipore	Grams/Mile Particulate: Glass Filter 1 cfm	Grams/Mile Particulate: Glass Filter 4 cfm
178A	4,285	2,200	FC Mod.	.0261	.0087	.0348	.0087	.0098

Additional Notes

1) This car did not start well, looking at the choke it did not appear to be closing completely. We were told by Phillips that this is the way it was designed to work.

2) The filter papers with the particulate collected on it were very light in color. Not at all like the 1971 Chevrolet, Federal Cycle cold start runs with choke on.

3) The dilution tube sweeping (particulate) did not resemble the usual type of material we have observed in the past. There was a sparkle to the particulate and the density was apparently very low.

4) All samples of particulate were given to the E.P.A. for analysis at Ann Arbor.

Continuation of Table 39

EXHAUST GAS ANALYSIS

Run No.	% by Volume				Parts per Million				Exhaust Condensate (ppm)	
	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x	HCHO.	NH_3
178A	-	-	-	-	-	-	-	-	3.6	5

Continuation of Table 40

EXHAUST GAS ANALYSIS

	% by Volume				Parts per Million				Exhaust Condensate (ppm)		ppm in Exhaust Gas	
Run No.	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x	HCHO	NH_3	HCHO	NH_3
203A	-	-	-	-	-	-	-	-	474.8	-	-	-
203B	11.7	5.2	81.8	.03	52	40	1650	-	266.3	19.6	15.7	2.0
203C	-	-	-	-	-	-	-	-	-	-	-	-
203D	-	-	-	-	-	-	-	-	-	-	-	-
203E	-	-	-	-	-	-	-	-	328.0	-	-	-
203F	-	-	-	-	-	-	-	-	-	-	-	-
203G	-	-	-	-	-	-	-	-	-	-	-	-
211A	-	-	-	-	-	-	-	-	363	9.26	-	-
211B	12.0	5.6	81.4	.03	66	40	1450	-	600	21.24	14.59	0.9

TABLE 40
CHASSIS DYNAMOMETER TEST OF CONVERTER EQUIPPED VEHICLES

Car Number: Environmental Protection Agency Lease 4065
Vehicle Type: 1972 Chevrolet 400 CID
Converter Type: PPG Trap Mufflers, etc.

Run No.	Car Miles	Converter Miles	Test Mode	Grams/Mile Particulate				
				Andersen Sampler	Millipore Filter	Andersen + Millipore	Glass Filter	
							1 cfm	4 cfm
203A	14,566	14,566	FC Mod.	.0520	.0650	.1170	.0625	.0550
203B	"	"	60 mph	.0150	.1880	.2030	.2124	.1791
203C	"	"	FC HS	-	-	-	.0666	.0517
203D	"	"	FC HS	-	-	-	.0733	.0500
203E	"	"	FC Mod.	.0782	.2217	.2999	.0978	.0586
203F	"	"	FC HS	-	-	-	.0800	.0516
203G	"	"	FC HS	-	-	-	.0667	.0483
211A	16,000	16,000	FC Mod.	.1043	.0174	.1217	.1054	.0619
211B	"	"	60 mph	.0134	.0907	.1041	.0933	.0826

Additional Notes

1) Water condensate which dripped out of the tail pipe connection during the test contained an orange-yellow colored solid material. An analysis of this material was conducted.

Phosphorus = <.3 ppm
Sulfur = .016%
Zn = .02%

Fe = .23%
Pb = .25%
Br = .20%

2) Run 211B - 60 mph steady-state was interrupted by two blown tires during the run. A full two-hour run was conducted with a 30-minute time interruption to change tires.

Continuation of Table 40

ANALYSIS OF EXHAUST PARTICULATE

Run No.	Trace Metals on Millipore Filter (%)											Measured in Particulate		
	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	% Pb Atomic Absorp	% C on Glass Filter	ppm BαP
203A	1.2	<.067	.43	.13	2.7	.65	<.067	.13	<.067	.24	<.067	39	33.9	180
203B	.004	<.002	.007	<.002	.016	<.006	<.002	<.002	<.002	.027	<.002	20.2	36.6	<1
203C	-	-	-	-	-	-	-	-	-	-	-	-	-	-
203D	-	-	-	-	-	-	-	-	-	-	-	-	-	-
203E	.32	<.02	.29	<.02	160	.10	<.02	<.02	<.02	.18	<.02	29.8	20.2	<24
203F	-	-	-	-	-	-	-	-	-	-	-	-	-	-
203G	-	-	-	-	-	-	-	-	-	-	-	-	-	-
211A	-	-	-	-	-	-	-	-	-	-	-	-	-	-
211B	-	-	-	-	-	-	-	-	-	-	-	-	-	-

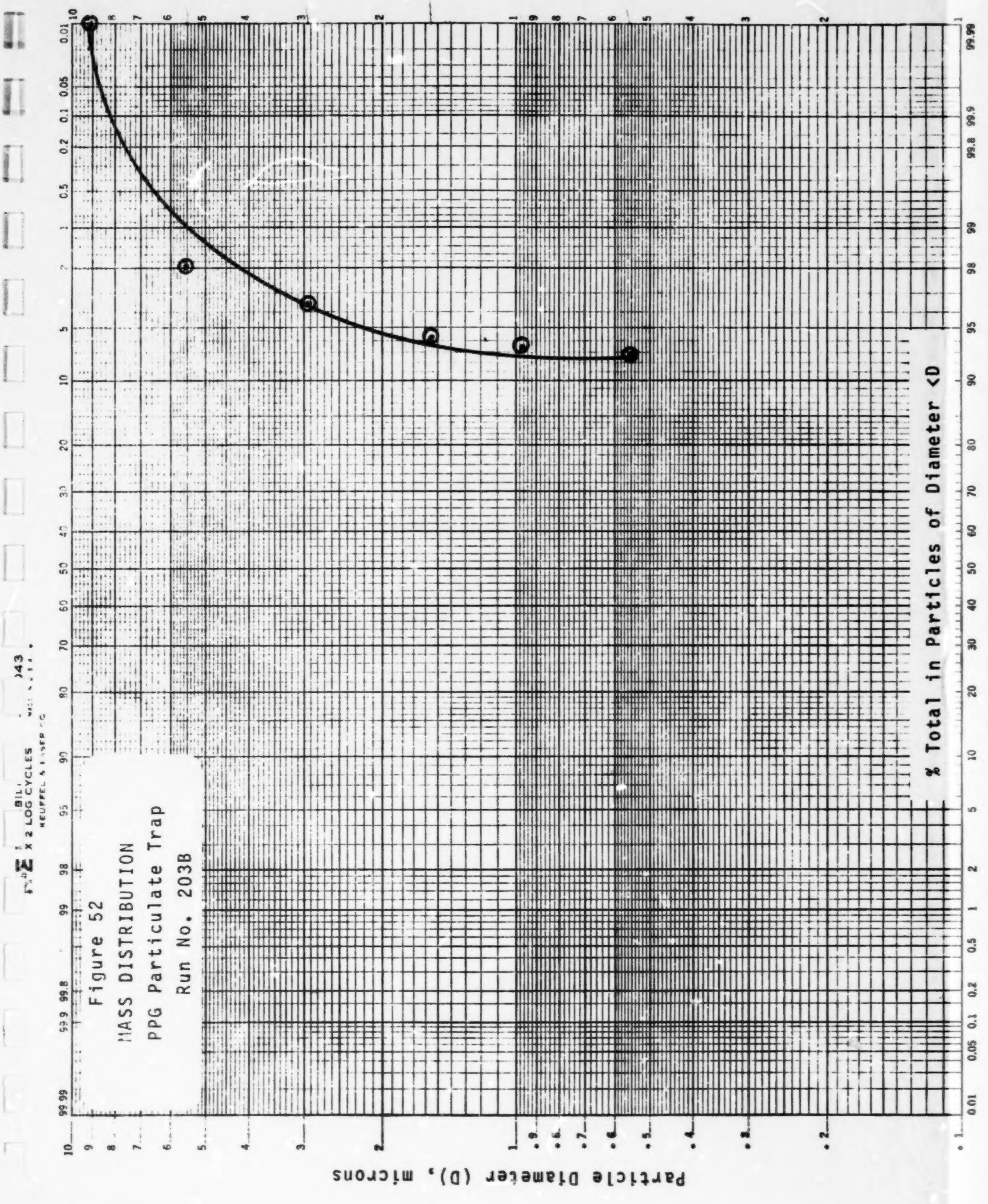


Figure 52
MASS DISTRIBUTION
PPG Particulate Trap
Run No. 203B

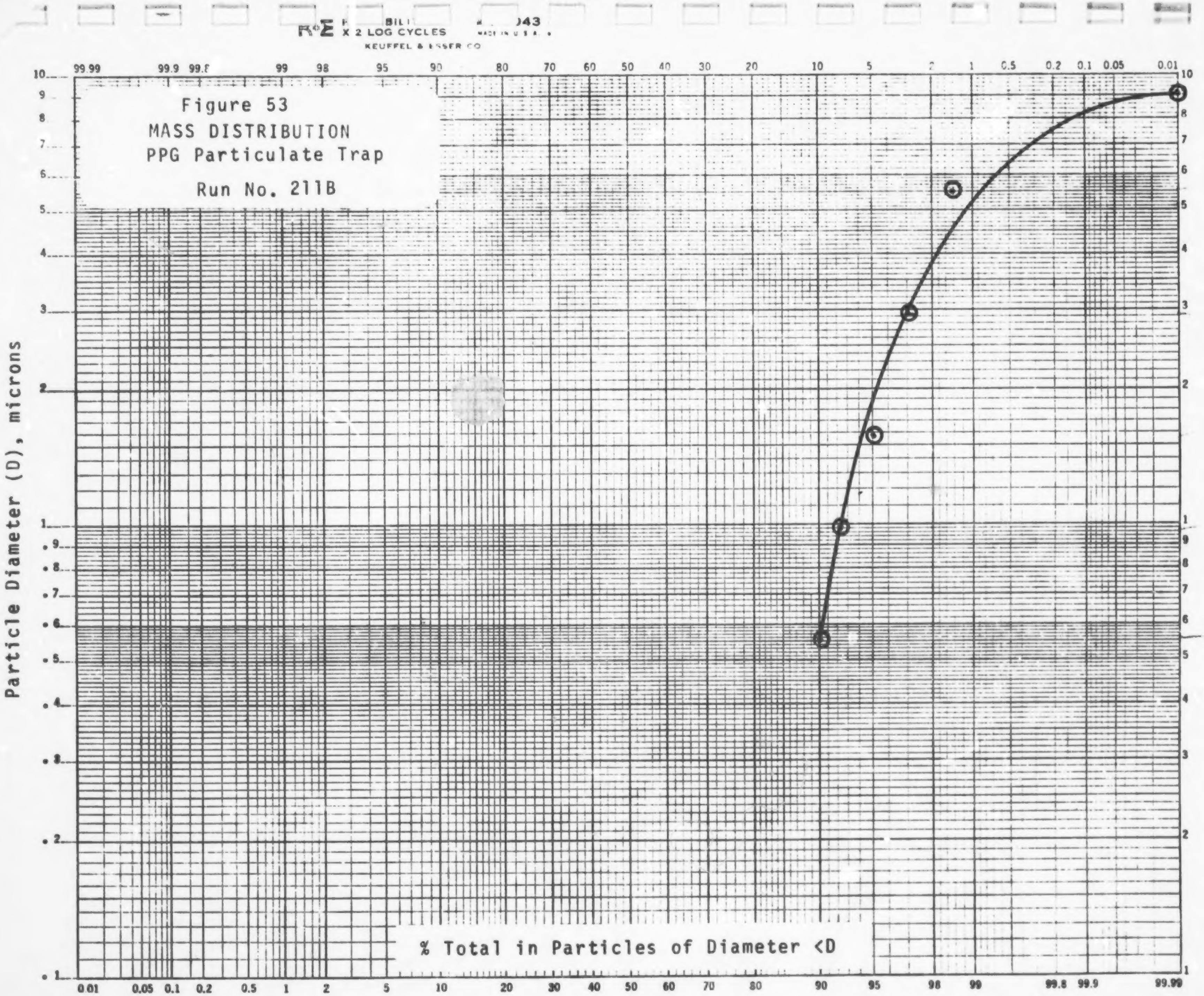


Figure 53
MASS DISTRIBUTION
PPG Particulate Trap

Run No. 211B

TABLE 41

CHASSIS DYNAMOMETER TEST OF CONVERTER EQUIPPED VEHICLES

Car Number: Environmental Protection Agency 801692

Vehicle Type: Mail Jeep Body

Converter Type: Stratified Charge Engine

				Grams/Mile Particulate				
							Glass Filter	
Run No.	Car Miles	Converter Miles	Test Mode	Andersen Sampler	Millipore Filter	Andersen + Millipore	1 cfm	4 cfm
219A	4,262	4,262	FC Mod.	.1043	.0217	.1260	.0283	.0358
219B	"	"	FC HS	.0999	.0199	.1198	.0500	.0533
219C	"	"	FC HS	.1066	.0267	.1332	.0666	.0516
219D	"	"	60 mph	.0091	.0756	.0847	.1046	.0942

Additional Notes

1) There was some question as to whether the engine was running right. It appeared to have a spark plug miss.

2) Dilution tube sweepings at the end of this series of runs #219A, B, C & D was 45.8 grams which is a gross amount compared to other vehicle tests. The sweepings were almost all magnetic indicating iron from the exhaust system. We were told this vehicle had not been run for a prolonged period which could account for the tube sweepings.

3) The test vehicle would not obtain 60 mph on the dynamometer so the test was conducted at 50 mph.

4) At 50 mph steady-state operation on the dynamometer there did not appear to be a miss in the engine.

Continuation of Table 41

EXHAUST GAS ANALYSIS

Run No.	% by Volume CO_2	O_2	N_2	CO	Parts per Million Total H.C.	NO_2	NO	NO_x	Exhaust Condensate (ppm) HCHO	NH_3	ppm in Exhaust Gas HCHO	NH_3
219A	-	-	-	-	-	-	-	-	33.7	5.4	-	-
219B	-	-	-	-	-	-	-	-	10.0	2.9	-	-
219C	-	-	-	-	-	-	-	-	-	-	-	-
219D	11.8	5.8	81.5	.02	10	7.0	230	-	10.3	3.3	0.6	0.35

Continuation of Table 41

ANALYSIS OF EXHAUST PARTICULATE

Run No.	Trace Metals on Millipore Filter (%)											Measured in Particulate		
	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	% Pb Atomic Absorp	% C on Glass Filter	ppm BaP
219A	2	.09	.9	.4	1	10	.2	.3	.10	-	.02	-	61.0	<31
219B	5	.13	.8	1.5	16	16	.3	.3	.15	-	.10	-	109.0	<10
219C	4	.006	.06	.09	12	.6	.03	.03	.006	-	.009	-	-	<31
219D	.03	.007	.03	.009	.3	.2	.006	.006	.01	-	.003	-	23.2	3.2
Tube Sweepings	40	.02	.03	.04	.005	.004	.2	.001	-	-	.005	-	-	-

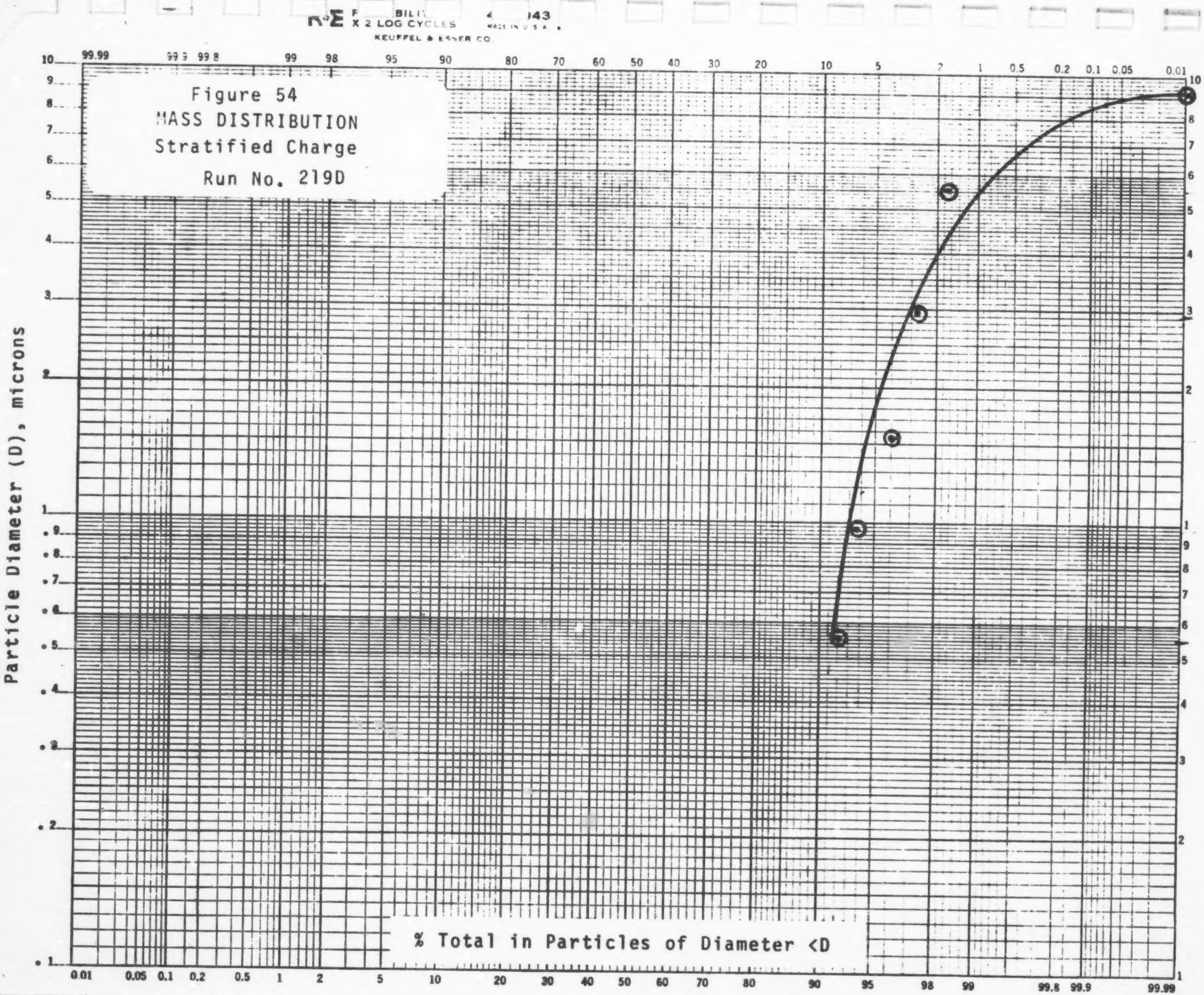


Figure 54
MASS DISTRIBUTION
Stratified Charge
Run No. 219D

TABLE 42

CHASSIS DYNAMOMETER TEST OF CONVERTER EQUIPPED VEHICLES

Car Number: Environmental Protection Agency
Vehicle Type: 1971 Pontiac
Converter Type: Questor Converter System

				Grams/Mile Particulate				
							Glass Filter	
Run No.	Car Miles	Converter Miles	Test Mode	Andersen Sampler	Millipore Filter	Andersen + Millipore	1 cfm	4 cfm
221A	8,000	8,000	FC Mod	(Tail pipe disconnect failure)				
221B	"	"	FC HS	.1399	.0133	.1532	.1600	.0883
221C	"	"	FC HS	.1333	.0266	.1599	.1533	.1049
221D	"	"	60 mph	.0083	.0104	.0187	.0292	.0175

Additional Notes

This car was driven on the dynamometer by the driver that delivered the vehicle. The choke on this vehicle. The choke on this vehicle was so adjusted so that it would not close completely and fuel was introduced at the carburetor to start it. No cold starts were conducted for this vehicle. Just hot starts and 60 mph steady-state.

Continuation of Table 42

EXHAUST GAS ANALYSIS

Run	% by Volume				Parts per Million				Exhaust Condensate (ppm)		ppm in Exhaust Gas	
No.	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x	HCHO	NH_3	HCHO	NH_3
221A	-	-	-	-	-	-	-	-	-	-	-	-
221B	-	-	-	-	-	-	-	-	2.1	97.7	-	-
221C	-	-	-	-	-	-	-	-	-	-	-	-
221D	10.7	7.7	80.6	.03	10	135	1760	-	.13	4.7	.007	0.4

Continuation of Table 42

ANALYSIS OF EXHAUST PARTICULATE

Run	Trace Metals on Millipore Filter (%)											Measured in Particulate		
No.	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	% Pb Atomic Absorp	% C on Glass Filter	ppm BaP
221A	8	.33	3.3	1.3	<25	>3	>.5	1	.10	-	.13	-	-	<5
221B	-	-	-	-	-	-	-	-	-	-	-	-	-	-
221C	3	.15	1.4	1.0	<12	>12	>.2	.3	.08	-	.05	-	5.1	-
221D	.6	.09	.52	.32	<2	>2	>.04	.2	.06	-	.02	-	4.5	<7
						-								
Tube Sweepings	25	15	.09	.2	.07	.02	.5	.5	-	-	.09	-	-	-

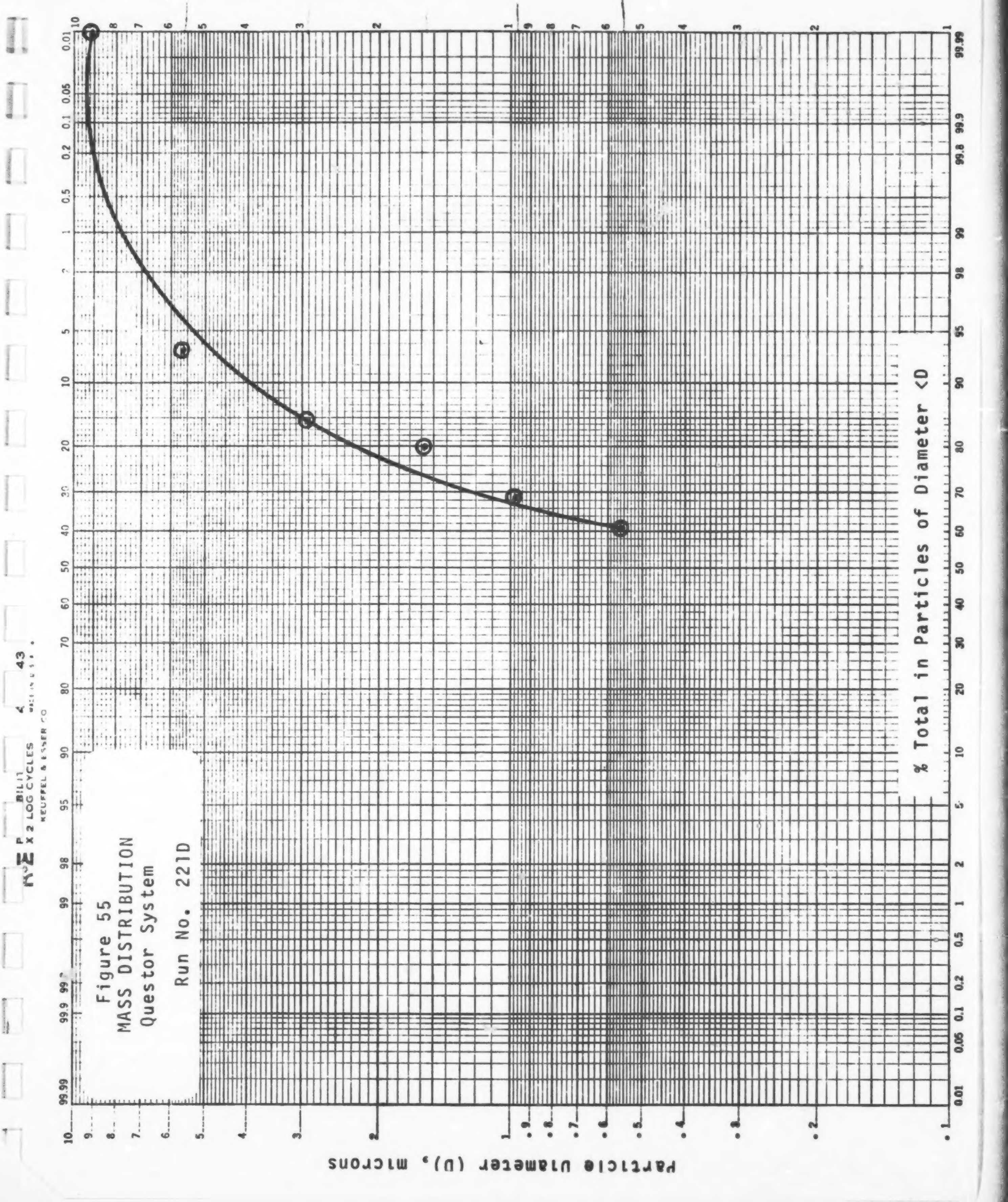


Figure 55
MASS DISTRIBUTION
Questor System

Run No. 221D

TABLE 43

CHASSIS DYNAMOMETER TEST OF CONVERTER EQUIPPED VEHICLES

Car Number: DuPont
Vehicle Type: 1970 Chevrolet
Converter Type: Thermal Reactor + EGR + Cyclone Collectors

Run No.	Car Miles	Converter Miles	Test Mode	Grams/Mile Particulate: Andersen Sampler	Millipore Filter	Andersen + Millipore	Glass Filter 1 cfm	Glass Filter 4 cfm
222A	11,376	2,000	FC Mod.	.1565	.0869	.2434	.0804	.0619
222B	"	"	FC HS	.0733	.1200	.1932	.0466	.0283
222C	"	"	FC HS	.0533	.1133	.1666	.0499	.0333
222D	"	"	FC Mod.	.0695	.0608	.1303	.0826	.0652
222E	"	"	60 mph	.0147	.0178	.0325	.0243	.0199
222F	"	"	60 mph	.0077	.0080	.0157	.0191	.0155
222G	"	"	FC Mod.	.1043	.2434	.3477	.1674	.1283
222H	"	"	FC HS	.1666	.1599	.3265	.0799	.0449
222I	"	"	FC HS	.1399	.1799	.3198	.1399	.1183

Additional Notes: See attached.

Additional Notes

Two different brands of fuel were used to make the series of runs.

(1) Run #222 A, B, C, D, E were made on the fuel the vehicle had in it when it was delivered. Supposed to be Sunoco #240.

(2) Run #222 F, G, H, I were made on Bay gasoline.

GASOLINE ANALYSIS

	Bay Gas	Sunoco #240
RVP	10.5	7.3
Gravity	57.4	59.1
I.B.P.	100.	96.
5% distillation	121.	115.
10%	148.	125.
20%	175.	148.
30%	192.	171.
40%	221.	196.
50%	238.	219.
60%	260.	240.
70%	280.	264.
80%	320.	301.
90%	370.	351.
95%	390.	400.
E.P.	415.	410.
RON	95.4	98.3
MON	84.8	87.0
Pb grams/gallon	3.30	2.34
Br grams/gallon	1.27	.91

Additional Notes

Two different brands of fuel were used to make The series of Runs.

(1) Run #222 A, B, C, D, E, were made on the fuel the vehicle had in it as it was delivered supposed to be Sunoco #240

(2) Run #222 F. G. H. I were made on Bey gasoline

Gasoline Analysis

	Bay Gas	Sunoco #240
RVP	10.5	7.3
Gravity	57.4	59.1
I. B. P.	100.	96.
5% distillation	121	115
10%	148	125
20%	175	148.
30%	192	171
40%	221	196
50%	238	219
60%	260	240
70%	280	264
80%	320	301
90%	370	351
95%	390	400
E.P.	415	410
RON	95.4	98.3
MON	84.8	87.0
Pb grams / gallon	3.30	2.34
Br " / "	1.27	.91

Continuation of Table 43

EXHAUST GAS ANALYSIS

Run No.	% by Volume				Parts per Million				Exhaust Condensate (ppm)		ppm in Exhaust Gas	
	CO_2	O_2	N_2	CO	Total H.C.	NO_2	NO	NO_x	HCHO	NH_3	HCHO	NH_3
222A	-	-	-	-	-	-	-	-	9.6	15.6	-	-
222B	-	-	-	-	-	-	-	-	1.8	1.85	-	-
222C	-	-	-	-	-	-	-	-	-	-	-	-
222D	-	-	-	-	-	-	-	-	5.3	.87	-	-
222E	13.1	3.7	82.3	.03	1	24	545	-	.5	.85	0.02	0.05
222F	13.5	3.1	82.5	.03	0	7.5	462	-	1.1	.87	0.07	0.09
222G	-	-	-	-	-	-	-	-	1.2	8.6	-	-
222H	-	-	-	-	-	-	-	-	-	-	-	-
222I	-	-	-	-	-	-	-	-	2.6	4.9	-	-

Continuation of Table 43

ANALYSIS OF EXHAUST PARTICULATE

Run No.	Trace Metals on Millipore Filter (%)											Measured in Particulate		
	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	% Pb Atomic Absorp	% C on Glass Filter	ppm BaP
222A	.7	.03	.4	.5	3	3	.05	.1	.02	-	.009	29.0	20.6	53
222B	.6	.03	.3	.4	3	3	.06	.1	.003	-	.008	13	10.6	120
222C	-	-	-	-	-	-	-	-	-	-	-	-	-	-
222D	-	-	-	-	-	-	-	-	-	-	-	-	-	-
222E	.5	.03	.7	.3	1	1	.02	.1	.01	-	.01	44	1.7	<3
222F	.6	.03	.6	.4	2	2	.04	.08	.02	-	.008	30	3.1	100
222G	2	.15	1.8	1.3	9	5	.2	.3	.19	-	.02	37	24.5	41
222H	.4	.01	.1	.2	2	1	.04	.05	.002	-	.004	13	18.8	-
222I	-	-	-	-	-	-	-	-	-	-	-	-	-	-

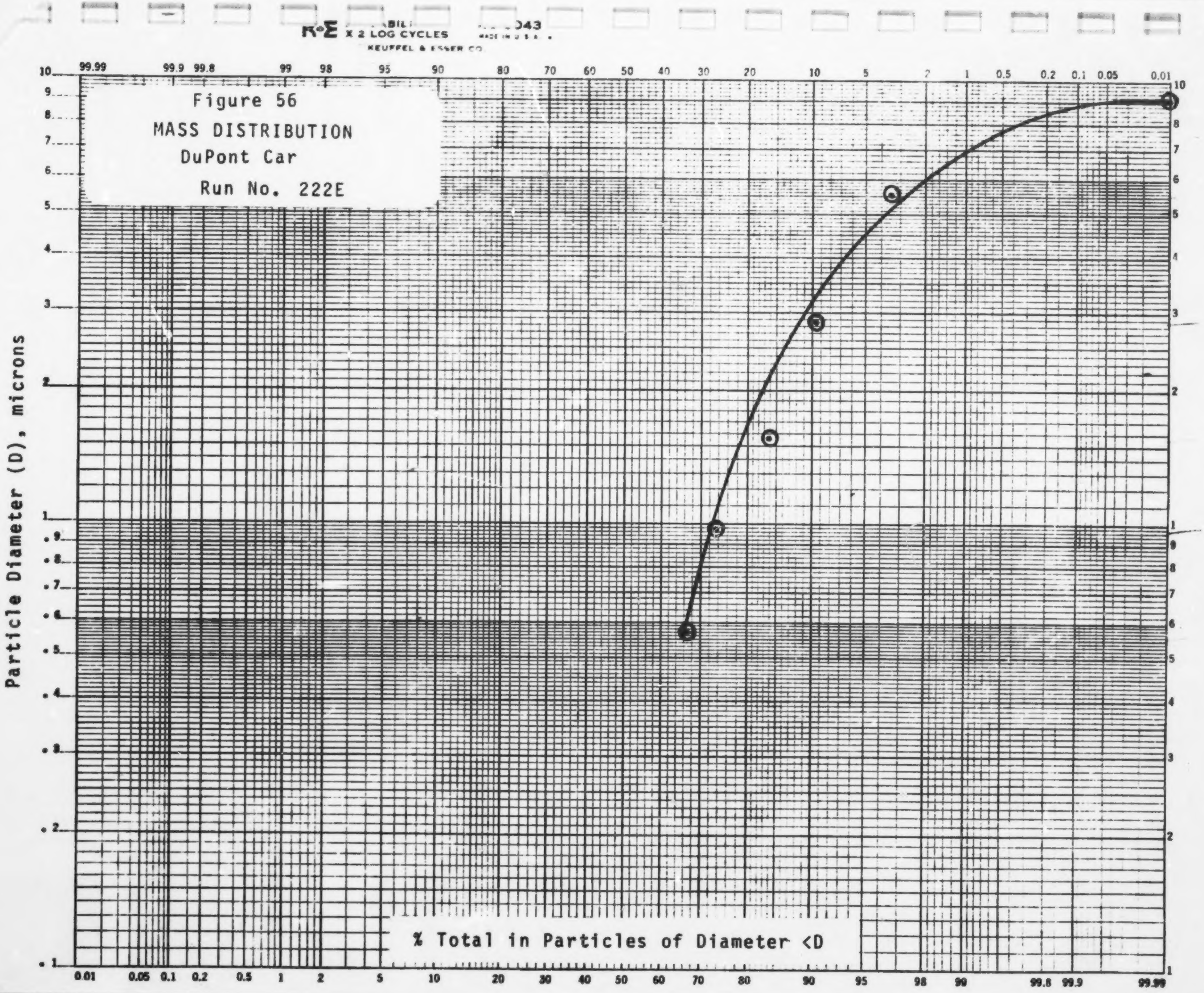


Figure 56
MASS DISTRIBUTION
DuPont Car
Run No. 222E

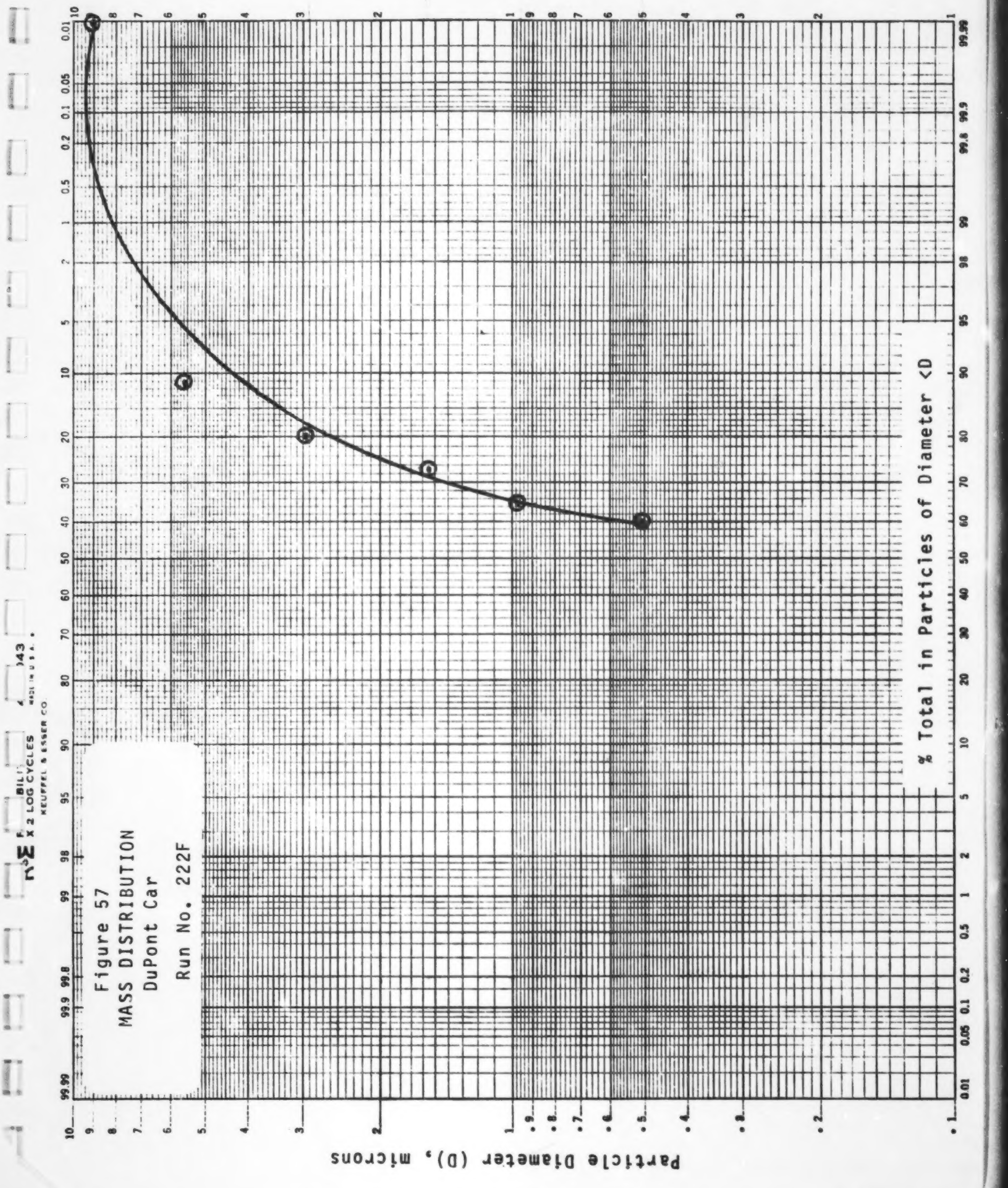
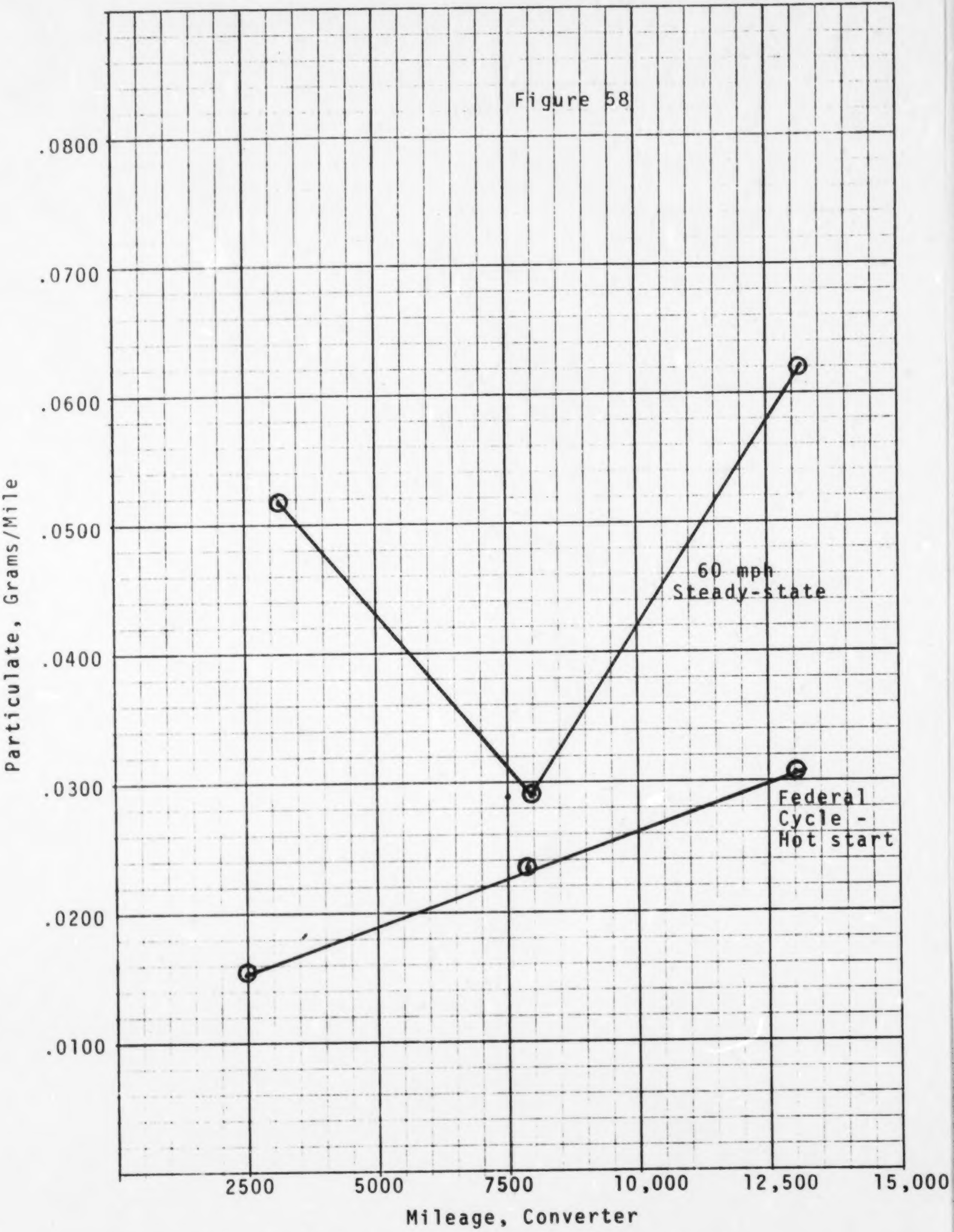
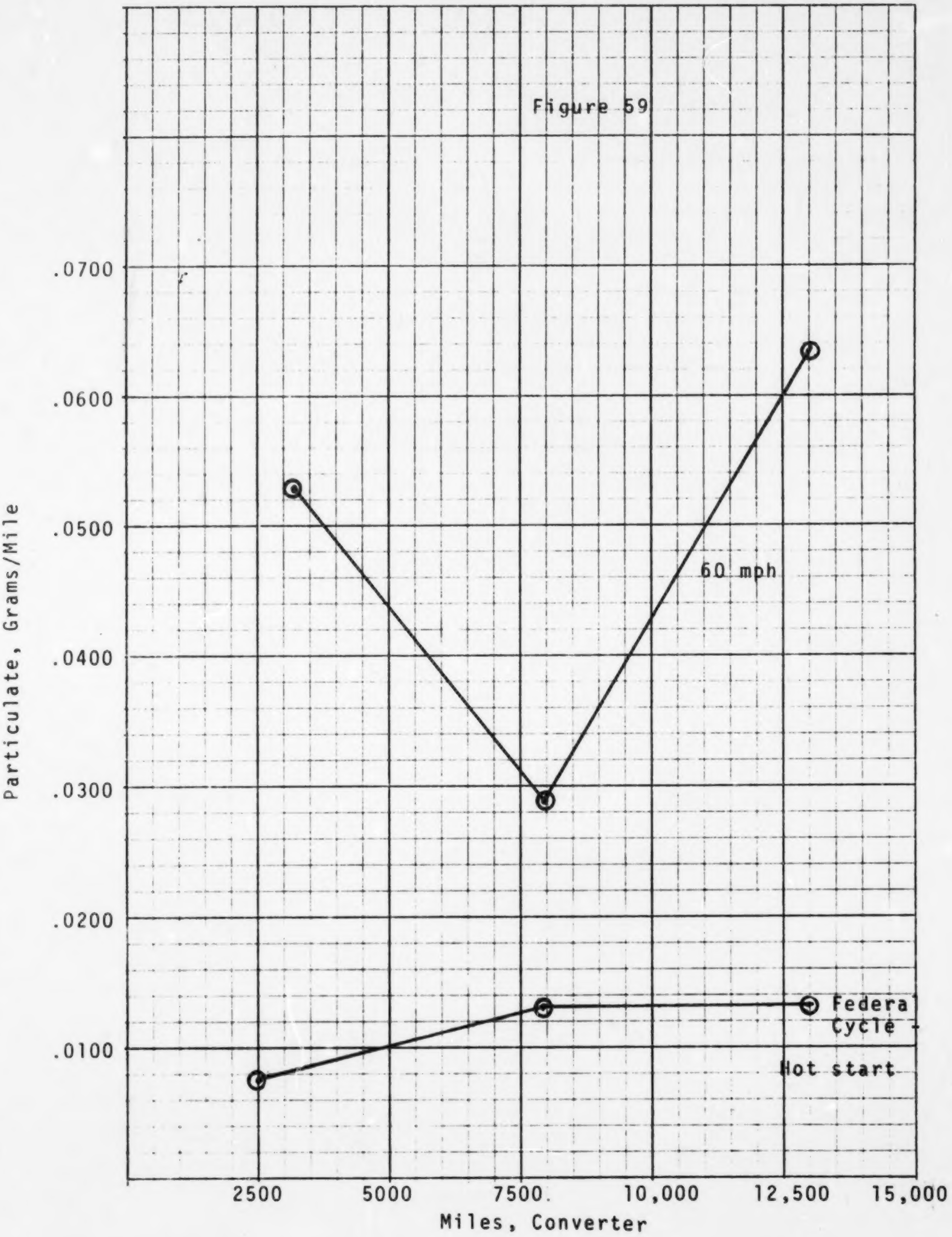


Figure 57
MASS DISTRIBUTION
DuPont Car
Run No. 222F

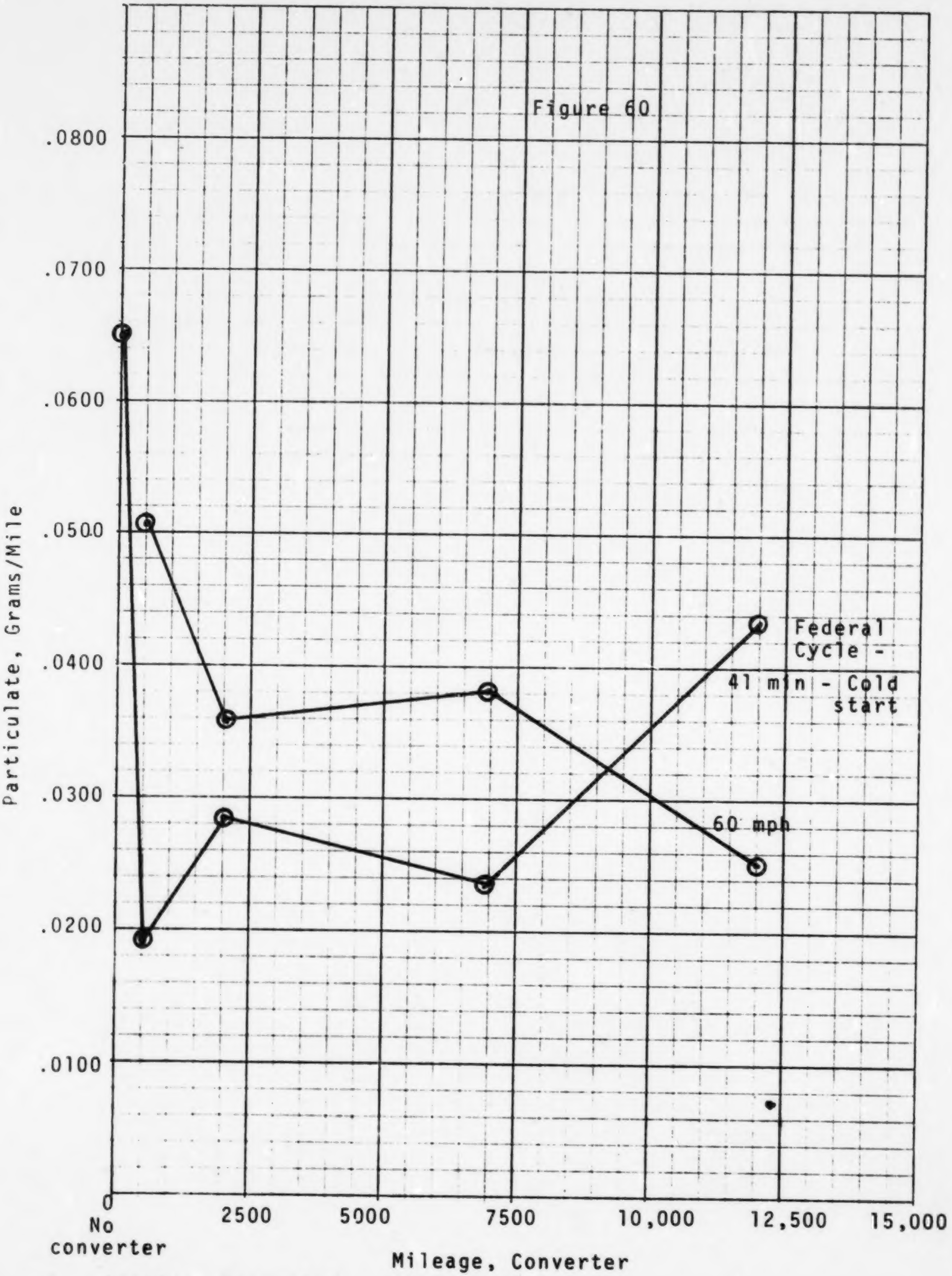


Car 61329, Basemetal, EGR - 142 mm filter, 4 cfm

Figure 59

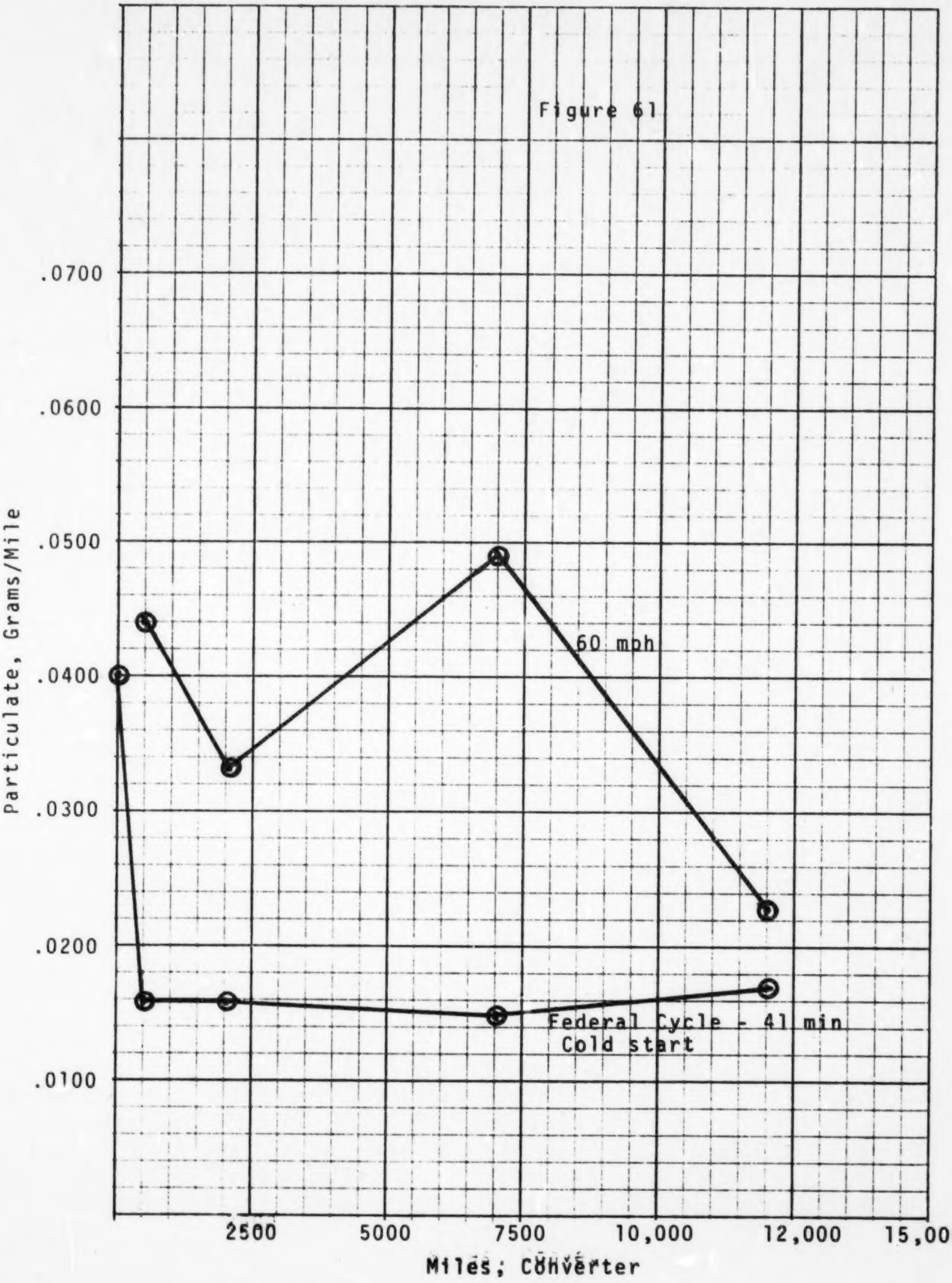


Car 61329, Basemetal, EGR - 142 mm filter, 4 cfm

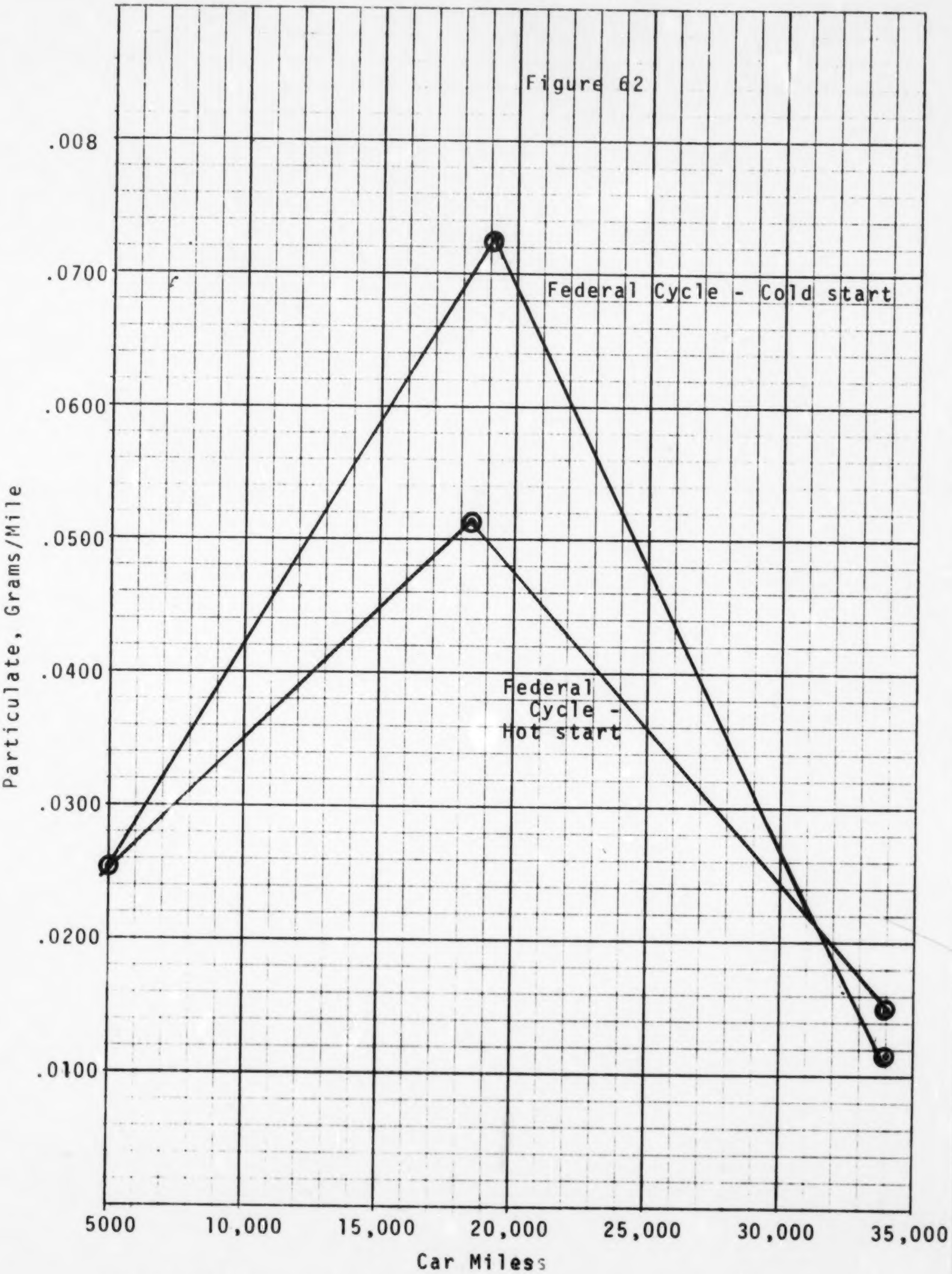


Pontiac, Basemetal - 142 mm filter, 1 cfm

Figure 61



Pontiac, Basemetal - 142 mm filter, 4 cfm



Car 61314, Noble Metal - 142 mm filter, 4 cfm

E. TASK V

Task V involved a preliminary look at some of the factors affecting the particulate mass sampling from a small, one-cylinder diesel engine. Table 44 is a summary of the specifications of the Labeco diesel used in the study. Figure 63 is a diagram of the dilution tube apparatus used for collecting the particulate.

The tube was designed to give 400 fpm flow rate of air and exhaust. This was roughly equivalent to what was used on the gasoline engine studies.

The first runs were made with the exhaust from the diesel entering the dilution tube at an orifice in the tube, hoping that the turbulence set up by the orifice would allow complete mixing. This proved to be unsatisfactory because of the large degree of the exhaust pulsation occurring with the one cylinder engine.

The pulsation effect was greatly reduced by introducing the exhaust into the dilution air stream counter to the air flow. The pulses were still strong enough, however, to necessitate the placement of the exhaust inlet at least 5 feet from the filter at the air inlet.

Only a few runs were made before the lack of time and funds forced us to stop. Several preliminary conclusions can be drawn:

1. The mass collected on the filter media, both millipore and glass fiber, was high enough to allow detailed analytical work on the particulate.

2. A single cylinder engine such as the one used in this work can be a valuable tool for diesel studies.

3. The size of the particles collected appears to be quite small, based on the figures in Table 45 showing the amount collected on the Andersen plates vs. the amount collected on the back-up Millipore filter.

TABLE 44
LABECO DI DIESEL, UNSUPERCHARGED

Bore:	3.80 in.
Stroke:	3.75 in.
Displacement:	42.53 cu. in.
Weight:	418 lbs
Compression Ratio:	16.7:1

Brake Torque at 1600 rpm	26.7
Brake Horsepower at 2800 rpm	11.8
BMEP at 1600 rpm	94
FMEP at 2800 rpm	56
FMEP at 2000 rpm	44
IMEP at 1600 rpm	136
ISFC at 1200 rpm	.365
BSFC at 1200 rpm	.511

TABLE 45
GRAMS/HOUR COLLECTED FROM A ONE CYLINDER LABECO DIESEL ENGINE
(1500 rpm, 900 grams/hr fuel consumption)

		Grams/Hour			
Run No.	Time	Andersen	Millipore Filter	Andersen + Millipore	Fiberglass Filter
214A	20 min	.0198	.0894	.1092	.1221
214B	60 min	.0036	.1494	.1530	.1378

Dilution tube flow rate was 400 ft/min, or 65 cubic feet per minute.

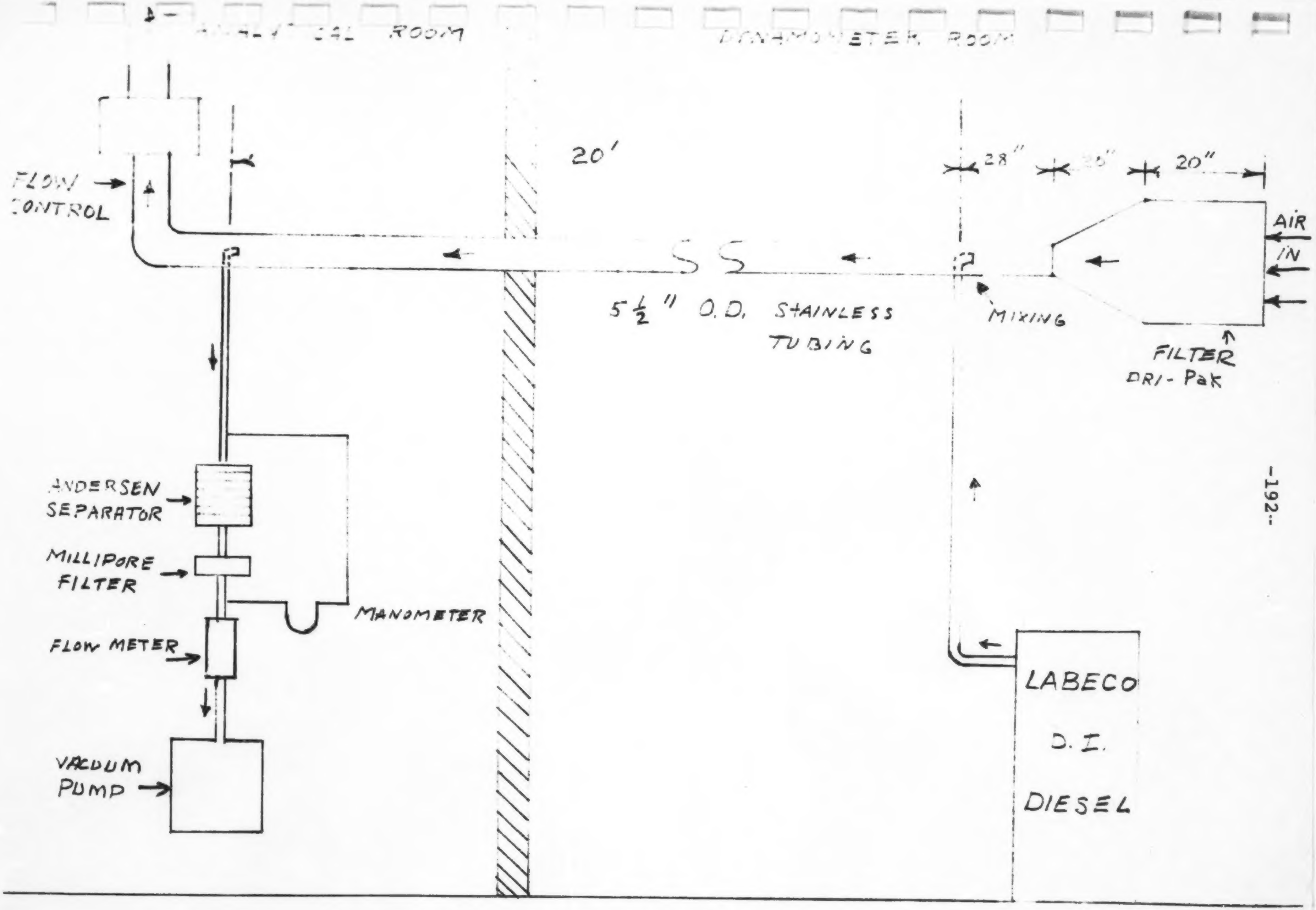

ANALYTICAL ROOM
DYNAMOMETER ROOM
20'
28"
30"
20"
AIR IN
FILTER DRI-Pak
MIXING
5 1/2" O.D. STAINLESS TUBING
SS
FLOW CONTROL
ANDERSEN SEPARATOR
MILLIPORE FILTER
MANOMETER
FLOW METER
VACUUM PUMP
LABECO D.I. DIESEL

FIGURE 63 - DIESEL DILUTION TUBE AND SAMPLING SET-UP

APPENDIX A

194

AN INVESTIGATION OF SOME VARIABLES OBSERVED WHEN SAMPLING PARTICULATE MATTER FROM AIR DILUTED AUTOMOTIVE EXHAUST

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and

Michael J. Baldwin

The Dow Chemical Company
Midland, Michigan

October 1971

SUMMARY

Both the quantity and quality of particulate matter* collected from air diluted automotive exhaust are affected by such variables as sampling temperature, dilution ratio, flow rate and by the presence of gasoline additives. An investigation of the effect of these variables is presented in this report.

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*Particluate matter is defined to be that nongaseous matter collected at filters under the sampling and operating conditions specified for each separate run described herein.

INTRODUCTION

In 1969 a study of the particulate emissions present in the exhaust effluent of automobile engines was initiated under a government contract at Dow. The problem at hand was to evaluate the effect of gasoline additives on the nature of such emissions. This necessitated the development of a reliable particulate sampling procedure. This procedure, described in a previous report[1] was found in duplicate tests to afford samples of particulate matter repeatable to within ±10% on a weight basis.

During the first year of the above program particulate samples were collected from the exhaust system of an internal combustion engine operating under controlled conditions on a dynamometer. The left bank of cylinders of a V8 engine was discharged via a convectional automobile exhaust system into a 27' x 18" polyvinyl chloride dilution tube where the exhaust effluent was diluted tenfold with filtered air. This condition permitted isothermal, isokinetic sampling of particulate matter at the end of the tube remote from the engine (See reference 1).

During the second year of the research program the results obtained in the above engine studies were related to those obtained for vehicles operating on a chassis dynamometer. Physical restrictions necessitated that changes be made in the particulate sampling procedure. A six hour sampling period was found to be the most practical as compared to a 48 hour period in the previous engine dynamometer studies. This reduction in sampling time would be expected to yield an eightfold reduction in weight of particulate matter collected. However during the chassis dynamometer studies the total vehicle exhaust was discharged to the dilution tube. An appropriate change in the air dilution ratio was made to afford the same overall flow rate within the dilution tube. Thus during the six hour sampling period and under otherwise identical sampling conditions it was expected that one fourth of the weight of particulate matter collected in the engine dyno runs would be collected during the chassis dynamometer tests.

This smaller weight of particulate matter proved inadequate for comprehensive analysis. It was therefore decided to supplement the Andersen sampler and filter combination operated at 1 cfm and used exclusively to this point of the program with an additional separate 142 mm filter operated at 4 cfm. One might expect the 4 cfm filter to collect four times the quantity of particulate matter collected at the 1 cfm Andersen and filter combination. In fact the

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[1] (See Government Report # CPA-22-45-145)

4 cfm filter collected from 20 to 70% less particulate matter than the ideal.

In view of the trend to nonleaded gasolines and the necessity for sampling particulate matter in the relatively short cycling sequences of the LA-4 and new Federal test procedures it was felt to be imperative that this anomaly be resolved and that the particulate sampling procedure be refined to afford meaningful and reproducible results under the above conditions.

APPARATUS

1.	Chassis Dynamometer	CLAYTON
2.	Engine Dynamometer	DYNAMATIC
3.	Andersen Sampler	
4.	Filter Holder	GELMAN
	a. Glass fiber filter	GELMAN
	b. Millipore membrane filter	
5.	Analytical balance	
6.	Electrical heated oven	
7.	Particulate collection system (See Figure #1)	

PROCEDURE

Details of the operating and sampling procedures are presented in Reference 1. All engines and vehicles were operated at the equivalent of 60 mph road load conditions.

1. Handling and Weighing of Filter Papers

The normal procedure for handling and weighing of filter paper was as follows:

a. The paper was stored in an air conditioned room at 75°F and weighed prior to use.

b. After sample collection the paper was weighed within minutes of removal from the filter holder and again when the weight had stabilized on the balance pan which was in the same air conditioned room at 75°F.

c. An experiment was conducted to evaluate the effect of heating on the weight of glass fiber filter pads. The results are presented in Figure #2. Since no weight loss occurred between the temperatures of 75°F and

100°F it was felt that the error in handling filter papers in the above manner was negligible.

2. Millipore versus Gelman Filter Papers

In most of the work a glass fiber filter was used. However in some incidents a membrane type filter was used to obtain particulate on a soluble substrate which could be used in various analytical procedures. It is important that both filter papers be equally efficient in particulate collection (Figure #3).

The data shows only a small difference in the efficiency of the two filters operating at 1 cfm flow rate. The difference could be a function of the fuel additive. The data presented includes no lead fuel and leaded fuel for comparison.

3. Exhaust Gas Velocity Through Filter Paper - 1 cfm vs. 4 cfm

If one compares a 1 cfm filter to a 4 cfm filter, the temperature of the exhaust gas in the 4 cfm filter is higher due to the shorter time it had in the sample line between the dilution tube and the filter. Consequently in order to compare the direct effect of flow rate on particulate collection the sample line leading to the 1 cfm filter had to be heated to maintain the same temperature as the 4 cfm filter.

As can be seen from Figure #4 there was a considerable loss in filter efficiency as the face velocity of the gas stream through the filter is increased. The exhaust particulate from leaded gasoline were less sensitive to filter flow rate than those from nonleaded fuel. This is probably due to a much higher level of volatile organics associated with nonleaded gasoline exhaust particulate.

4. Exhaust Gas Temperature at Filter

It is not surprising that the temperature of the filter would have a pronounced effect on the amount of particulate matter collected on the filter (See Figure #5). Again the use of nonleaded gasoline has a greater effect on the percent of particulate retained as the filter temperature is increased. As was also expected the mild cycling conditions show the greatest percent change due to the lower boiling materials one would expect in the exhaust gas.

5. Leaded Fuel Versus Nonleaded Fuel

The percent of lead in the gasoline had a definite effect on the difference in the particulate pick-up on the 1 cfm filter plus Andersen sampler versus the 4 cfm filter only (See Figure #6).

A tabulation of the runs that were made at 60 mph road load steady state operation show that the particulate matter collected from leaded gasoline exhaust is the least sensitive to changes in sampling procedure.

It is felt that the increasing differences observed with the reduction of lead in the fuel are due to the increased level of volatile organics associated with the particulate matter resulting from the combustion of nonleaded fuel. The face velocity on the filter and the higher operating temperature of the 4 cfm filter would have a greater tendency to remove the more volatile compounds.

6. 1 cfm Filter Plus Andersen Sampler Versus 1 cfm Filter Without Andersen Sampler

A comparison was also made between the efficiency of the 1 cfm filter alone and the 1 cfm filter used in conjunction with an Andersen sampler. With leaded gasoline the difference in efficiency varies from 2.8 to 13.9% (See Figure #7). Using nonleaded gasoline the efficiency of the two systems varies from 39.5 to 82.4%. Of particular significance is the fact that the Andersen sampler collects 70 to 80% of the particulate matter compared to the 1 cfm filter when using nonleaded fuel. However when leaded fuel is used the Andersen sampler accounts for only 35 to 40% of the particulate matter collected. It is felt that the difference in collection efficiency between nonleaded fuel and leaded fuel is again due to the high ratio of volatile organics present in the particulate matter from the nonleaded gasoline. The magnitude of the thermal drop across an Andersen sampler is similar to that of a filter so one would expect to collect more particulate on the combined 1 cfm filter/Andersen system.

7. Thermal Profile of Sampling System

The data tabulated in Figure #8 shows the average thermal drop across a 1 cfm filter to be 36.4°F and that across a 4 cfm filter to be 12.7°F. The temperature drop across the Andersen sampler was found to be 17.4°F and that across the combined Andersen and 1 cfm filter to be 53.8°F.

8. Unbound Water in Two Types of Filter Media Before and After Particulate Collection

In order to assess the possible effect of unbound water on the weights of particulate matter collected a glass fiber and millipore filters, both types of filter pads were desiccated both prior to and after sample collection. The data is tabulated in Figure #9.

It was found that the glass fiber filter has a very low water retention this was the main filter used for the particulate collection studies to date. The membrane filter was very susceptible to water pick-up and must be used with caution.

CONCLUSIONS

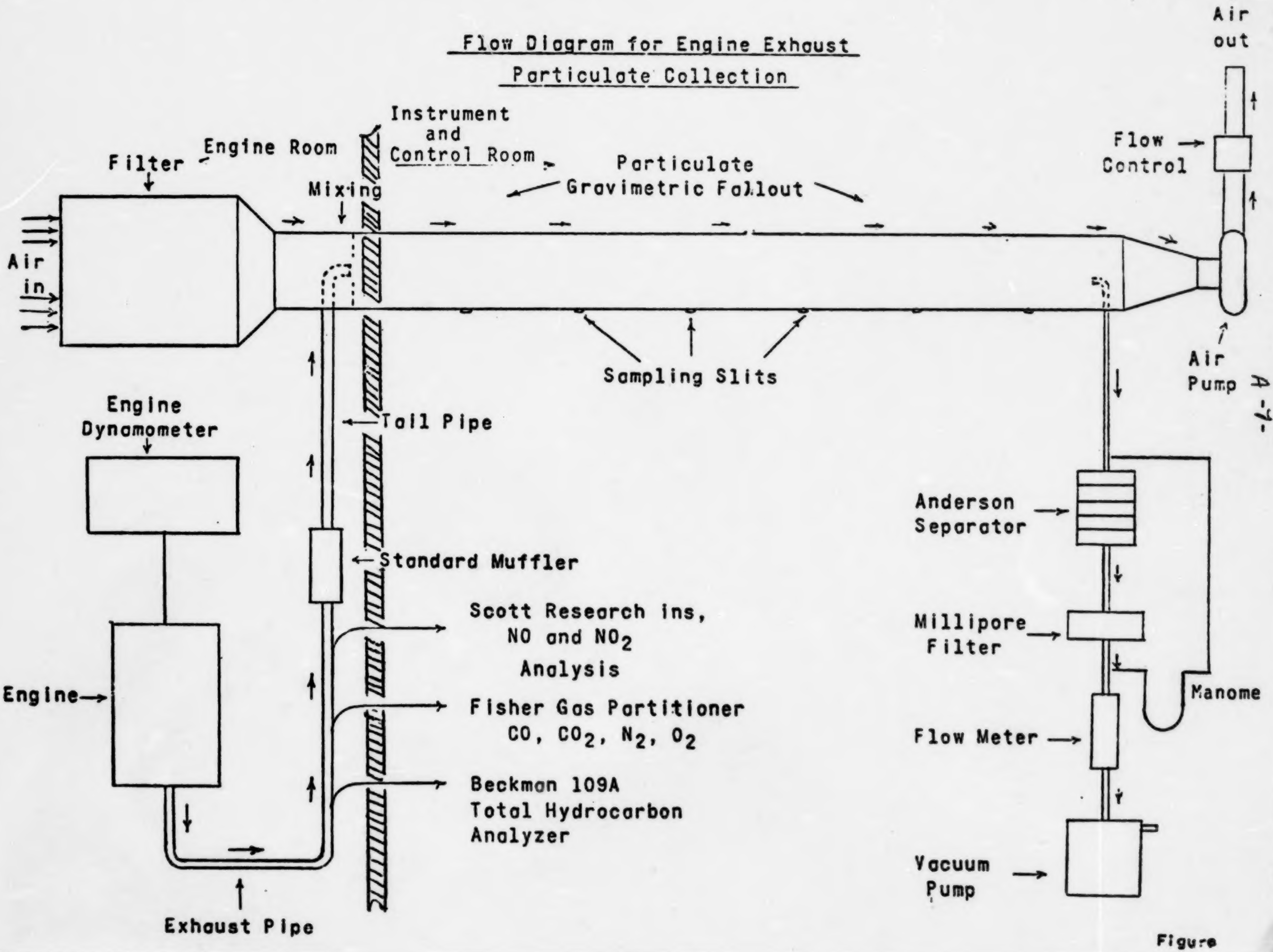
1. The temperature of the diluted exhaust gas has a significant effect on the quantity of particulate matter collected in the sampling system described in this report.
2. The flow rate of the exhaust gas being sampled through a filter paper was found to have a definite effect on the amount of particulate collected on the filter paper.
3. Fuel additives such as TEL have an effect on the efficiency of particulate collection system as a result of changes in particulate composition.
4. The major filter media used for particulate collection was glass fiber filter with no binders. This type of filter media presented no gross problem if proper handling and weighing procedures were followed.

RECOMMENDATIONS

1. The effects of exhaust gas dilution ratio, dilution air moisture content, dilution air temperature, and residence time in the dilution tube are other factors that should be studied as to their effect on the collection of particulate emissions.
2. Any definition of particulate matter must be referred to a very well defined set of sampling parameters.

Flow Diagram for Engine Exhaust

Particulate Collection


Air out
Instrument and Control Room
Filter
Engine Room
Mixing
Particulate Gravimetric Fallout
Flow Control
Air in
Air Pump
Sampling Slits
Engine Dynamometer
Tail Pipe
Standard Muffler
Scott Research ins, NO and NO_2 Analysis
Fisher Gas Partitioner CO, CO_2, N_2, O_2
Beckman 109A Total Hydrocarbon Analyzer
Engine
Exhaust Pipe
Anderson Separator
Millipore Filter
Manome
Flow Meter
Vacuum Pump

Figure

FIGURE #2

TYPE "A" GLASS FIBER FILTER #61698 142 mm

All temperatures were held for one hour
before weighing. Six papers were used
to check reproducibility

	Filter Paper No.					
Temperature °F	#1	#2	#3	#4	#5	#6
Wt. grams at 75°	.9341	.9572	.9404	.9565	.9471	.9453
Wt. grams at 100°	.9341	.9572	.9404	.9565	.9471	.9453
Total grams loss	.0000	.0000	.0000	.0000	.0000	.0000
Wt. grams at 150°	.9338	.9567	.9400	.9564	.9467	.9450
Total grams loss	.0003	.0005	.0004	.0001	.0004	.0003
Wt. grams at 200°	.9335	.9563	.9398	.9557	.9464	.9444
Total grams loss	.0006	.0009	.0006	.0008	.0007	.0009
Wt. grams at 250°	.9333	.9563	.9396	.9557	.9464	.9444
Total grams loss	.0008	.0009	.0008	.0008	.0007	.0009

The six filter papers were returned to storage
room over weekend and reweighed

Start wt. grams at .75°	.9341	.9572	.9404	.9565	.9471	.9453
48 hrs. wt. grams at 75°	.9340	.9570	.9403	.9564	.9471	.9449
Permanent wt. loss grams	.0001	.0002	.0001	.0001	.0000	.0004

FIGURE #3

SAMPLING

Same Exhaust for Same Time Period
Flow Rates on All Filters 1 cfm

	Millipore #AAWP 14200 AA 0.8 μ pore size White Plain 142 mm Membrane Type	Gelman Glass Fiber Filter Type A - 142 mm 99.7% Efficient for Removal of .3 μ particles	Change %
Run #44 Nonleaded Fuel	.0402 grams	.0377 grams	-6.2
Run #75 Leaded Fuel	.0652 grams	.0701 grams	+7.0

FIGURE #4

DILUTED EXHAUST PARTICULATE FILTRATION

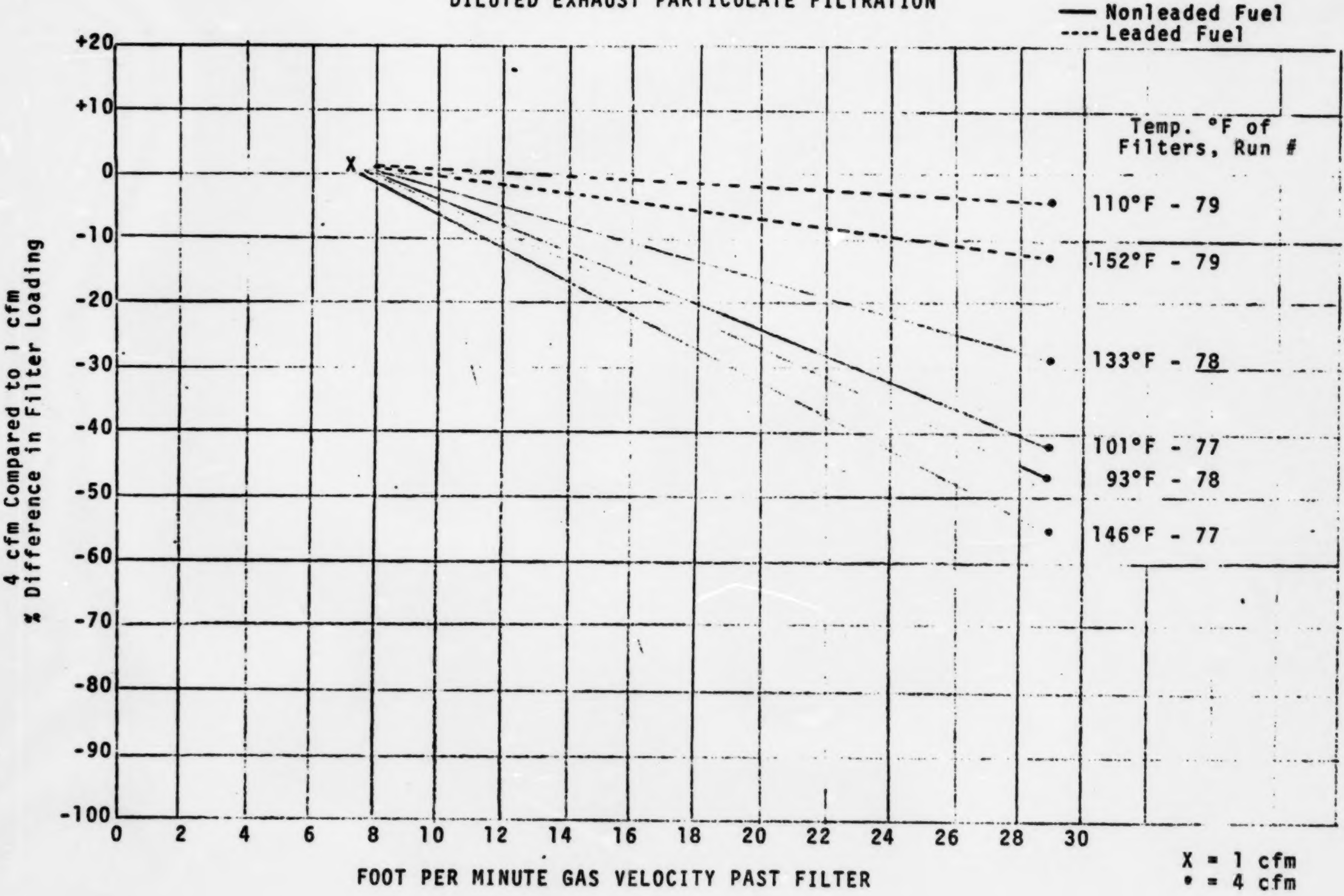


FIGURE #5

DILUTED EXHAUST PARTICULATE FILTRATION

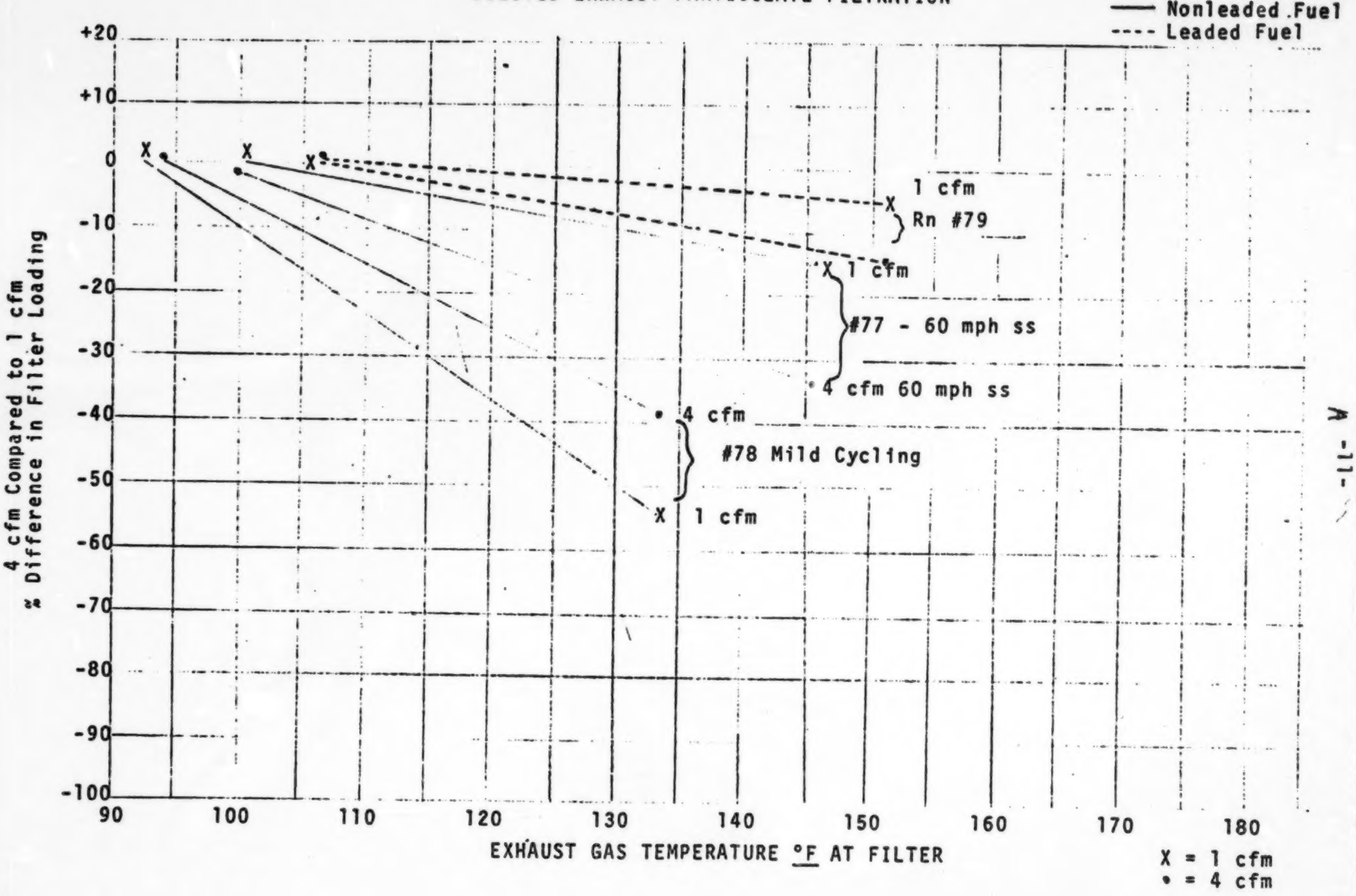


FIGURE #6

The effect of leaded gasoline on the difference in particulate pick-up on the 1 cfm filter and Andersen versus 4 cfm filter only.

TEL in Gasoline	Number of Runs Averaged	Percent Less Particulate Collected on 4 cfm Filter Compared to 1 cfm Filter and Andersen
None	6	-72.23%
.5 cc/gal.	4	-40.60%
3. cc/gal.	9	-19.29%

FIGURE #7

Leaded Gasoline			Particulate Grams Per Mile		
Run #	1 cfm Filter	Andersen	Total	1 cfm Only	% Change 1 cfm Filter Compared to 1 cfm & Andersen
80	.0117 (60.6%)	.0075 (38.8%)	.0193	.0166	-13.9%
	.0121 (65.0%)	.0065 (39.6%)	.0186	.0164	-11.82%
81	.01228 (64.0%)	.0069 (35.9%)	.01918	.01826	-4.7%
	.01253 (66.5%)	.0063 (33.4%)	.01883	.01883	-2.8%
Nonleaded Gasoline					
82 Millipore Glass	.0010 (14.4%)	.0057 (82.6%)	.0069	.0012	-82.4
	.0019 (30.10%)	.0044 (69.8%)	.0063	.0038	-39.5%

FIGURE #8

THERMAL PROFILE OF SAMPLING SYSTEM

Chassis dynamometer 60 mph steady
state with air to exhaust dilution
ratio between 4:1 and 6:1

		Temperature °F			
Run #	CC of TEL	Of Sample	1 cfm	Andersen Plus 1 cfm Filter	4 cfm Filter
50	3.0	167.2		81.5	143.5
58	0.0	144.2		92.0	142.0
61	0.5	147.0		90.0	137.0
67	3.0	147.2		87.5	136.1
70	0.5	141.4		84.3	132.0
72	0.0	139.0		82.4	126.0
75	3.0	156.6	108.	86.0	139.
77	0.0	116.7	101.0		102.2
78	0.0	-	92.7		93.6
79	3.0	125.2	105.1		117.0
80	3.0	131.8	103 105	86 86	
81	3.0	129.8	108 106	88 86	
82	0.0	128.4	98.6 104.0	82 82.4	
Avg. Temp, °F =		139.5	103.1	87.5	126.8

FIGURE #9

DESICCATOR STUDY OF FILTER PAPER

		Tare	New Tare After 48 hrs. in Desiccator	Moisture Loss
Millipore Filters	#1	3.2961 gm	3.2883 gm	.0078 gm
	#2	3.2945 gm	3.2868 gm	.0077 gm
Glass Fiber	#3	1.1226 gm	1.1223 gm	.0003 gm
	#4	1.1321 gm	1.1318 gm	.0003 gm

		Immediately After Particulate Collection	New Tare	Particulate	After 24 hrs. in Desiccator	Moisture Loss
Millipore Filter	#1	3.3019 gm	3.2883 gm	.0136 gm	3.2959 gm	.0060 gm
	#2	3.2984 gm	3.2868 gm	.0116 gm	3.2925 gm	.0059 gm
Glass Fiber	#3	1.1296 gm	1.1223 gm	.0073 gm	1.1294 gm	.0002 gm
	#4	1.1394 gm	1.1318 gm	.0076 gm	1.1392 gm	.0002 gm

		After 48 hrs. in Desiccator	Moisture Loss
Millipore Filters	#1	3.2934 gm	.0085 gm
	#2	3.2919 gm	.0065 gm
Glass Fibers	#3	1.1293 gm	.0003 gm
	#4	1.1390 gm	.0004 gm